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THE RANCIDITY PROBLEM AND NEW DEVELOPMENTS WITH PARTICULAR REFERENCE TO THE EFFECT OF LIGHT [1]

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Introduction

Few research problems have been more perplexing to chemists than the one dealing with the deterioration of oils and fats due to rancidity. Spoilage from this source amounts to millions of dollars annually. Notwithstanding the enormous amount of valuable research devoted to the subject, only recently has it been shown that certain wave lengths of light promote rancidity more rapidly than others.

According to Pool (1931), Davies (1931), and others, rancidity may be divided into three types, namely, ketonic, hydrolytic, and oxidative. This article deals with the oxidative type, which is believed to be developed wholly or in part by contact with air, light, heat, moisture, metals, and possibly enzymes. By rancidity as here discussed is meant that characteristic odor and taste which are produced by exposure of an oil or fat to light or to the action of metals. Often a distinct lardy odor is a forerunner of this state of decomposition or change.

Color Tests

The various angles of attacking this problem of rancidity may be shown by a brief review of the literature. It is conceded by Powick (1923) and others that some of the degradation products evolved as an oil becomes rancid are peroxides, aldehydes, ketones, and acids and that they are formed as a result of the addition of molecular oxygen to the unsaturated double bond.

Qualitative tests for aldehydes have thus been devised which are dependent on the formation of color, the intensity of the color being a

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measure of the degree of rancidity. Kreis (1902), Von Fellenberg (1924) (who slightly modified Schiff's test), Kühl and Klemt (1930), Kerr and Sorber (1923), and more recently Schibsted (1932) are well known workers in this field. Numerous objections to the use of these color tests for the detection of incipient rancidity have been made. Davidsohn (1930), Davies (1930), Cooke (1929), and others consider that tests by taste and odor afford evidence of deterioration long before it can be detected by any chemical test.

Powick (1923) made a systematic search among the known degradation products of oleic acid for the substance or substances characteristic of the rancid condition and found that epihydrin aldehyde was responsible for the Kreis reaction. He also made spectroscopic comparisons of colored condensation products of phloroglucin obtained from a rancid cottonseed oil and from a non-rancid cottonseed oil which gave a Kreis test. No similarity could be observed. However, such tests are at present being relied upon for the purpose of examining an oil.

Fatty Acids

Browne (1899), one of the early workers on the causes of rancidity, found that in the development of rancidity in butter-fat, the first products formed were aldehyde substances and that these were further oxidized to acids. He also states that with the increase of free fatty acids in the case of rice bran and of butter, rancidity progresses. Ritsert (1890) and Spaeth (1896) made use of the increase of fatty acids as a measure of the development of rancidity. DeConno and Dragoni (1925) corroborated Ballantyne's (1891) statement that fatty acids are not the cause of rancidity, although an increase in their amount is accompanied by the development of rancidity in some cases. Scala (1897), Schmid (1898), Solstien (1898), Mayrhofer (1898), and Amthor (1899) believed that the characteristic odor and taste of rancidity comes from the subsequent transformation products of the fatty acids, aldehydes, and ketones. Duclaux (1887) and Ritsert (1890) showed clearly that micro-organisms have no influence on the development of oxidative rancidity and concluded that the process must be chemical in nature.

Triebold and Bailey (1932) in their extensive work on the keeping qualities of shortenings and crackers state that the free fatty acid content of a fat does not necessarily denote the stage of rancidity development. They further state that it is indicated from a survey of the literature that fatty acids should be considered as possible catalysts in the process of rancidity development. The outstanding investigations supporting this idea are those of Greenbank and Holm (1924), who found

that free fatty acids catalyzed the autoxidation of butter-fat, those of higher molecular weight exerting the greatest catalytic effect.

Triebold and Bailey (1932a) conceived the idea subsequently that the fatty-acid content might indicate the keeping quality of the fat or oil, and to test out their theory they conducted experiments using samples of lard of varying fatty-acid content. The length of their induction period of oxygen absorption was considered a measure of keeping quality of the fat. Their results showed that the free fatty acid determination is of significance, but it cannot by itself be used as an index of the keeping quality of a fat because no regular progression in decreased length of the induction period with increasing acidity was observed.

Paul I. Smith (1930) makes substantially the same assertion. Reinmann (1900), Kerr and Sorber (1923), and Stokoe (1921) likewise found that there was no direct relation between the amount of the acid formed and the extent of rancidity. Henry L. Smith (1915) also believes that rancidity does not run parallel with acidity.

As far back as 1915 Vintilesco and Popescic (1915) observed that acidity is not a necessary accompaniment of rancidity and, therefore, reasoned that fats could undergo an additive reaction with molecular oxygen. Holm, Greenbank, and Deysher (1927) and also Davies (1930) hold that the method of treatment of the oil or fat is a major factor in the stability of cottonseed oil to oxidation. They give as an example crude cottonseed oil, which was higher in acidity than any of the grades of refined oil which showed the greatest resistance to oxidation.

Lea (1931), who has recently been studying the effect of light on the development of rancidity, found that oxidation in the presence of light appears to have little effect upon the free acidity of the fat and that no detectable increase in acidity could be observed as the effect of low contents of active oxygen or peroxides.

It is evident from the results of these investigators that acidity of oils or fats has no direct relation to the development of rancidity.

Iodine Number

It would seem that the iodine number of oils might show a relationship between fats that easily become rancid, since the mechanism which brings about the development of rancidity is believed to be the addition of oxygen to the unsaturated glyceride. However, it is explained by Triebold and Bailey (1932, 1932a) that each kind of fat is composed of unsaturated types of glycerides which may be selectively oxidized. Pool (1931) found that the iodine value decreased with the development of rancidity, but the difference between the fresh and rancid oils was too small to be of any service in the measurement of rancidity.

Davies (1930) states that advanced stages of deterioration are necessary before any appreciable and significant change in the iodine value of the oil is noticeable. Holm, Greenbank, and Deysher (1927) found that there is no relationship between the iodine number and the susceptibility of cottonseed oil to rancidity. After various treatments, Guthrie (1917), in experiments with butter which had been exposed to high temperature and light, found no change in the iodine number.

Metals

Emery and Henley (1922) established by their extensive investigations that metals have a strong catalytic action on the development of rancidity. They found that in the presence and in the absence of light, lard containing strips of copper had become very rancid in 56 days, while lard without the metal but protected from light showed no rancidity at the end of that time. Other experiments by these same authors concerning the rate of production of rancidity in fats stored in various atmospheres of air, oxygen, and carbon dioxide revealed that in an atmosphere of oxygen, both in the presence and absence of a metal, rancidity developed at an earlier date, and progressed more rapidly than in samples held in an atmosphere of carbon dioxide or in air. The fats in carbon dioxide and in air became rancid in about the same length of time.

The results of their experiments showed that lard in contact with metals developed rancidity even when the metal itself was apparently not attacked. On the other hand, rancidity did not develop in the lard not in contact with a metal when the lard was protected from light. It was further shown that oils in contact with copper developed rancidity more rapidly than those in contact with the other metals used. Those in contact with tin and aluminum were the least affected. Emery and Henley extended their experiments further to include the value of protective coatings on metal, having in mind metallic containers for fats and oils. Their results showed that a continuous and unbroken coating of lacquer upon a metallic container effectually prevents the action of the metal in promoting rapid production of rancidity.

Davies (1928) six years later pointed out that metallic catalysts, such as iron and copper, very strongly favor oxidation; in fact, such catalysts appear to be far more powerful in action than any of the other contributing causes of rancidity. Minute traces of metallic salts, especially those of copper, iron, and manganese, even as low as one part of these metals per million of fat or oil, cause an appreciable shortening of the induction period as shown in tests with butter-fat and butter. Davies goes so far as to say that copper acts as an oxygen carrier as well as a liberator of

nascent oxygen, copper being twelve times as active a catalyst to oxidation as iron.

Hunziker and Hosman (1917), in their work relating to tallowy butter, have also experimentally demonstrated that catalytic agents such as metals or metallic salts in butter or butter-fat act as oxygen carriers and cause rancidity in a short time. Copper and alloys of copper, for example, brass and German silver, are the most active metals and alloys used in machinery for commercial butter making.

Peroxides

While almost every theory on the oxidation of fats and oils postulates the formation of peroxides when molecular oxygen attacks the double bond in an unsaturated fat, only recently have workers attempted to use this peroxide oxygen as a quantitative measure of the deterioration of an oil or fat. Powick (1923), Tschirch and Barben (1924), Heffter (1904), Holde, Bleyberg, and Brilles (1931), and others have used it qualitatively.

Heffter showed that rancid fats which contain peroxides will liberate iodine from potassium iodide solution; later Taffel and Revis (1931), and Lea (1931) studied this same reaction from a quantitative aspect. Wheeler (1932) subsequently modified and improved Lea's procedure whereby a homogeneous mixture of the oil, solvent, and potassium iodide could be obtained and the reaction made more rapid, complete, accurate, and much less cumbersome. This modification has proved of considerable value to the oil industry since it is possible to calculate ahead of time from a curve made of those particular oils studied, when any one of the oils is expected to turn rancid. More recently Kilgore (1933), Royce (1933), and King, Roschen, and Irwin (1933) have further improved Wheeler's method as a means for following the induction period of an oil.

Light

Many investigators have definitely found that light plays an important rôle in the development of rancidity. Browne (1925) conducted experiments to measure the rate of change in weight of butter-fat which, over a period of years, had been exposed to light and to darkness. During the nine years of the experiment the butter-fat exposed to light exhibited a uniformly greater percentage increase in weight than the fat which was kept in darkness. Kerr (1921) concluded as the result of a series of tests of different fats and oils stored under controlled conditions of light, temperature, and access of air, that under no conditions does rancidity occur in the absence of oxygen but that when oxygen is

present either heat or light will accelerate rancidity. It is his claim that moisture, especially in the presence of light, promotes spoilage of fats and that copper and zinc are more active catalyzers for the development of rancidity than tin, aluminum, or iron. Kerr (1921) and Emery and Henley (1922) and others found that storing oils or fats in the dark noticeably delayed the development of rancidity.

Salkowski (1917) asserts that rancidity is due to the combined activity of atmospheric oxygen and light, the speed of the process depending upon the intensity of light. He found that in the absence of light very little oxygen is consumed. These findings corroborate those of Ritsert (1890).

Davies (1932), in discussing the development of taint in oil-bearing foodstuffs, concludes that light is one of the serious causes of spoilage and emphasizes the necessity of taking strict precautions at all stages of manufacture to guard against undue exposure to strong sunlight. He further states that although the effects of strong light in shortening the induction period may not be at once apparent, he has found that once autoxidation has been initiated the subsequent storage of the product in the dark does not in any way arrest its development.

Lea (1931) has conducted a more elaborate investigation of the effect of light on the oxidation of fats than any other investigator up to the present time. The points covered in his investigation were the relative susceptibilities of fats to oxidation, the effect of various intensities of illumination, the autocatalytic nature of oxidation, the differences in susceptibility to oxidation, the bleaching action of light, and the influence of oxidation on free acidity.

In order to follow these changes during oxidation Lea found that it was necessary to have a quantitative knowledge of the state of oxidation in the specimens of fat; to be able to detect and follow the earliest stages of deterioration; and last, to possess the means of comparing the potential keeping qualities of any two or more fats. This information was obtained by applying a new test for the development of rancidity which consisted in estimating the amount of peroxide formed during the autoxidation of the fat. The peroxide determination furnished a means of obtaining the rate of increase of the active oxygen in the course of the breaking down of the fat.

By eliminating light almost entirely (98%) it was possible to reduce oxidation or peroxide formation by fully 75%. In other words, when the oil was exposed to intense light the peroxide value after 400 hours was approximately 23, whereas when the light intensity was reduced to only 2%, the peroxide value was less than 5. With complete elimination of light, the peroxide value was less than 0.5. It would seem, therefore, that a very small amount of light (even as low as 2%) is

sufficient to exert an appreciable influence on the rate of oxidation of an oil, and once oxidation has begun, removal of the light source does not reduce the rate of oxidation to that of the unexposed fat, the reaction proceeding in the absence of light at a rate depending upon the amount of active oxygen already present.

The following conclusions taken from Lea's article are very significant in connection with the theory that rancidity is essentially a photochemical phenomenon:

> Oxidation is accelerated sensibly by weak artificial light, while exposure for a few minutes to direct sunlight is sufficient to produce rancidity.
>
> The reaction is autocatalytic and even brief exposure to light accelerates the subsequent oxidation.

It is even claimed by Wagner, Walker, and Oestermann (1913) that light alone, in the absence of air, is capable of producing rancidity. This is possibly explained by Holm, Wright, and Greenbank (1927) who say that the keeping quality of samples stored in vacuum is largely dependent upon the inherent quality of the fat, the nature of which is due to some type of loosely bound oxygen, which cannot be removed by vacuum and which is sufficient to cause perceptible odors and flavors when it oxidizes the fat.

Preliminary Experiments

In view of the action of light in causing rancidity, it occurred to us that possibly certain wave lengths of light were more responsible than others for inducing this form of spoilage. In order to try out this idea, various colored cellophanes bought on the market served, in a limited way, as color filters.

Our first experiments (Coe, 1932, and Coe and LeClerc, 1932) made use of rice bran and rice polish, two products which turn rancid quickly. They were enclosed in pink, red, purple, blue, yellow, green, black, and clear wrappers, and exposed to sunlight. At the end of a week or ten days the samples were tested with the Von Fellenberg reagent. All samples gave the intense color reaction indicative of rancidity, except the samples wrapped in green or black. This experiment clearly showed that the various wave lengths of light behave differently with respect to the development of rancidity and that green better than any other color seemed to exert a protective action against this change.

In many experiments that followed, color filters covering the range of the visible spectrum, each having a definite and known light transmission were employed. Foil and also black paper which exclude all light, were also used. In all samples exposed to a certain shade of green called "sextant green," embracing wave lengths between 4900

and 5800 Ångström units, rancidity was delayed for a much longer period of time than in samples exposed to light transmitted by other filters. Black paper and foil, of course, were better than color filters because all wave lengths were excluded. Sextant green, which was found to show the best protection against the development of rancidity, is essentially the same shade as luxuriant green grass or chlorophyll. Signal green (blue green) and yellow green were not so effective. The former allows violet and blue wave lengths to be partly transmitted; the latter transmits in part yellow, orange, red and infra-red wave lengths.

Among the oil-bearing foods irradiated with light transmitted by these various color filters were salad oils, butter, lard, rice bran, rice polish, whole-wheat flour, self-rising flour, peanut butter, shelled nuts, coffee, potato chips, corn-meal, mayonnaise, crackers, and cookies. In every case those samples protected by green or black kept free from rancidity for a comparatively long period while those irradiated by other wave lengths of the visible spectrum became rancid much sooner. These experiments again clearly established that certain wave lengths of light play a definite and important rôle in the development of rancidity.

Some work was done with a monochromator, an instrument so constructed with a quartz prism that a substance can be irradiated with definite wave lengths of light. Fresh butter, being an article which turns rancid quickly and which is most suitable for use with this instrument, was spread on a glass plate the size of a lantern slide and irradiated with light from a mercury lamp, which produces bands at 3020, 3130, 3650, 4060, 4358 and 5461 Ångström units. After 17 hours exposure to these wave lengths, the samples were tested with the Von Fellenburg reagent. Butter exposed to every wave length gave the characteristic magenta color indicating rancidity except that exposed to the band at 5461 Ångström units, which is practically at the peak of the true green.

Another sample of fresh butter was spread on a plate and irradiated with a 500-watt Mazda lamp, which furnishes energy covering wave lengths from 5200 to 10,000 Ångström units. This experiment was conducted with a light source of the same intensity as in the first experiment. The butter this time was irradiated for 96 hours instead of 17. Tests for rancidity were made and positive color reactions obtained. They were weaker, however, than those obtained with the ultra-violet and blue end of the spectrum.

As a result of the work with the monochromator it is evident that yellow, orange, red, ultra-violet, violet, and blue hasten the development of rancidity as compared with green and infra-red. The green and infra-red appear to be photochemically inert so far as effect on rancidity is concerned.

The Effect of Moisture and Air

In one experiment rice bran was placed in each of two clear glass bottles, one being wrapped with black paper so that no light could shine on the material inside. Both were provided with a means to circulate air through the sample while being irradiated by light from a window. After ten days the samples were tested. The bran protected by black paper remained fresh, whereas the one in the clear bottle was appreciably rancid. This experiment was repeated, but in addition two more sets were included. One set contained powdered metallic iron and the other powdered copper-oxide, as catalysts, and the bottles were provided with circulating air and placed in the window. In about two weeks only those samples kept in the clear bottles were rancid. Emery and Henley (1922) showed in the case of lard that presence of metals caused rancidity even in the dark. Our experiments with rice bran showed that in the presence of metals there was no development of rancidity in the absence of light.

Another experiment was conducted with rice bran in which dry ice was used to replace all air present. A large piece of dry ice was placed in each of four Mason jars containing rice bran. Two jars were wrapped with black paper. The others remained unwrapped. These samples were exposed to the winter light of a southern window. When an unwrapped sample, serving as the control, became rancid the experimental samples were examined. Those wrapped in black were perfectly fresh; the ones in clear jars were rancid. The atmosphere of carbon dioxide apparently in no way tended to protect the rice bran when it was placed in sunlight. Here again light is shown to be a main factor in the development of rancidity. This experiment bears out the findings of Ritsert (1890), Emery and Henley (1922), and Holm, Wright, and Greenbank (1927).

Another experiment showing the effect of light was conducted with corn oil both before and after frying of potato chips. The samples of both oils were divided, one part was protected with a black wrapper which thus excluded all light; the other, enclosed in white manifold paper, was exposed to direct sunlight. Weekly peroxide tests were made of these oils. The values were plotted as shown in Figure 1. After standing some months, the oils protected by black wrappers were still free from rancidity, while those wrapped in manifold paper were very rancid.

Experiments with other oil-bearing foods such as cottonseed oil, lard, butter, and corn oil were conducted, using Corning color filters, and in each case only those products from which all light except sextant green and sextant red were excluded remained free from rancidity.

Potato chips were placed in green, black, and clear paraffin packages and exposed to western sunlight. After one month's exposure the chips wrapped in green or black were still edible, while those in the clear package were rancid within one week.

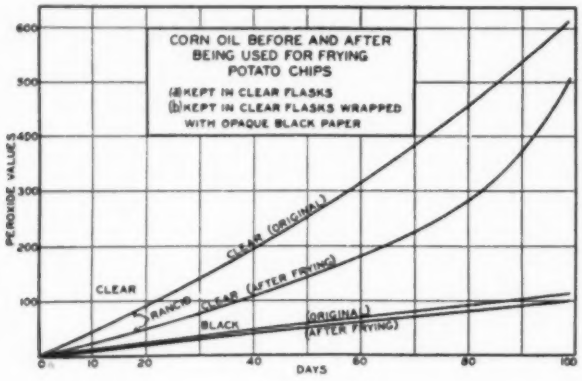

Fig. 1.

For the purpose of comparing the efficacy of green glass with green paper wrappers on the market, the following foods were placed in special green glass bottles furnished by the Corning glass works: peanut butter, pecan meats, cashew meats, butter, lard, salad oil, potato chips, rice bran, and salted crackers. Samples of these same foods were likewise placed in bottles of clear glass. All these samples were exposed on the roof during September.

After one day's exposure the freshly prepared potato chips in the clear flask were rancid. The same was true with both butter and lard. The other articles in the clear flasks showed signs of rancidity in about four days with the exception of peanut butter, which became rancid in about ten days. All the commodities in the green flasks remained fresh for several months.

Other experiments have been conducted which show conclusively that certain wave lengths of light play an important rôle in the development of rancidity. At this stage of our work Wheeler published a method of following the progress of rancidity by determining the amount of the peroxides evolved. Experiments were therefore planned in order to determine the influence of selective light on the formation of peroxides in various oils and fats. Oils and fats were placed in bottles wrapped both with opaque black paper and with protective green paper, as well as in blue and in clear unwrapped bottles and allowed to stand exposed to diffused light as reported by Coe and LeClerc (1933).

The results of these experiments indicate that when an oil has been protected from light by green or opaque wrappers or in tin containers

positive reactions with the well-known color tests for rancidity used at the beginning of this investigation, and the peroxide test for the oxidation of an oil do not necessarily prove that the oil is rancid. For example, corn oil protected from light as already mentioned did not give organoleptic tests for rancidity after seven months, although it gave strong positive tests with both the Kreis and the Von Fellenberg reagents and at the same time showed relatively high peroxide values. (See Figure 2.)

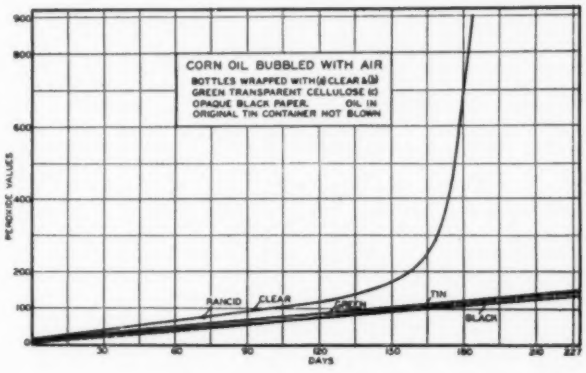

Fig. 2.

An unprotected oil generally becomes rancid when its peroxide value has reached approximately 60 millimoles per liter. In the case cited above the protected oil reached even a higher peroxide value without showing any organoleptic signs of rancidity.

Similar results have been obtained with oils exposed in the same way with the exception that air was bubbled through it at the rate of 6 liters per hour for a period of several weeks. Oil which had been protected from light, and which had developed a high peroxide value without becoming rancid, became rancid when exposed to light after removal of the protective wrapper. The results of our experiments would apparently support the view that oxidative rancidity may be due principally to photochemical action on a compound which either exists independently in the oil or is produced from compounds which give rise to the formation of peroxides.

To investigate further the influence of various wave lengths of light on peroxide formation and on the development of rancidity, cottonseed oil was placed in each of twelve crucibles which were proof against all light except that furnished by the color filter that covered it (Coe and LeClerc, 1933). All samples were placed on the inner sill of a closed south window. The color filters were so selected and arranged that

they absorbed certain known wave lengths of light until the whole visible spectrum had selectively been utilized for irradiation. It was possible thus to observe the effect of the different wave lengths of light on the oil. Lard, in another experiment, was irradiated in the same manner.

The results of these experiments with the cottonseed oil and lard, given in Table I, show that light of the blue end of the spectrum is more

TABLE I

PEROXIDE VALUE AND RANCIDITY [1] OF SELECTIVELY IRRADIATED COTTONSEED OIL AND LARD

Color of filter	Transmission falls to 5% — Angström units	Cottonseed oil [2]			Lard [3]	
		May 9	May 18	June 28	July 25	August 26
Clear	3100	314.9 vr	472.2 vr	801.0 vr[4]	54.7 r	305.2 vr[4]
Blue	5600	86.7 r	275.0 vr	837.0 vr[4]	0.5 nr	331.0 vr
Tinted yellow	4000	78.4 r	77.5 r	538.8 vr	0.4 nr	197.0 vr
Little darker yellow	4150	72.3 r	73.5 r	200.8 vr	0.4 nr	40.7 r
Still darker yellow	4410	64.9 r	65.1 r	106.5 r	0.4 nr	39.6 r
" " "	4650	47.0 nr	59.4 r	97.9 r	0.3 nr	lost
" " "	4840	45.2 nr	57.0 r	95.5 r	0.2 nr	18.0 r
" " "	5150	38.7 nr	51.7 nr	lost	0.1 nr	23.8 r
Special green	5090	26.8 nr	34.7 nr	75.1 nr	0.1 nr	0.3 nr
Orange red	5650	35.9 nr	47.6 nr	76.4 sr	0.1 nr	0.7 sr
Medium red	6120	28.9 nr	39.6 nr	75.2 sr	0.1 nr	0.6 sr
Far red	6310	29.3 nr	39.7 r	81.1 r	0.1 nr	19.1 r

[1] Organoleptic test expressed thus:
vr = very rancid
r = rancid
sr = slightly rancid
nr = not rancid

[2] Original peroxide value 14.8 on April 26.
[3] Original peroxide value 0.1 on July 14.
[4] Also viscous.

conductive to the formation of peroxides and the development of rancidity than that of the red end for the same time of irradiation. Also there seemed to be an acceleration in the formation of peroxides and in the development of rancidity in proportion to the amount of blue light transmitted by the filter. The experiment with lard suggests that animal fats show relatively the same response to selective light as do vegetable oils in the development of both peroxides and rancidity. The color which promoted rancidity the least was green delimited by 4900 to 5800 Ångström units. These findings are somewhat different from those of Greenbank and Holm (1933) who showed that blue light was the least effective in producing oxidation. It should be stated, however, that their oils were irradiated with light of equal energy.

Discussion

Sufficient work has been done to show that light plays a very important rôle in the development of rancidity. The question arises, however, why does green light, delimited by 4900 and 5800 Ångström units, have the least harmful action on oil-bearing foods?

According to Bancroft (1908):

> Those rays which act chemically on a substance must be absorbed by it, and the chemical action of light is closely connected with the optical absorption. Each color of the spectrum can have an oxidizing or reducing effect, depending on the nature of the light-sensitive substances. In all cases, the chemical action of light comes under the law that those rays are most effective which are absorbed by the light sensitive substances.

(This is illustrated in Figure 3.)

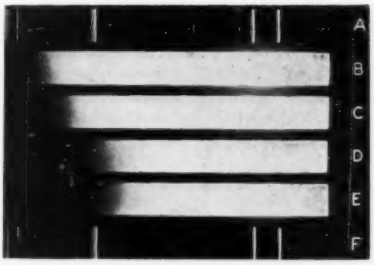

Fig. 3. Spectra of oil samples protected from light.
A, F. Spectrum lines of mercury arc.
B. Spectrum of Mazda light source.
C. Transmission of rancid oil.
D. Transmission of nonrancid oil.
E. Transmission of fresh oil (not aërated).

A number of examples of the oxidizing action of light on organic substances may be found in the literature. Bancroft further suggests that the action of light consists in bringing about a change in the dissociation conditions or in the loosening of certain valences. In so doing the substance is brought into a more reactive condition by producing a system which contains unsaturated active portions with free valences, occasioned by a molecular change in structure, a change in the dissociation relations, oxidation and decomposition products, or by a molecular rearrangement.

When, therefore, oil-bearing foods subject to rancidity are enclosed by green of a proper shade, the deleterious wave lengths of light which cause rancidity are absorbed by the wrapper or container instead of by the light sensitive substance which causes the characteristic spoilage. On this basis it is reasonable to believe that the substance causing deterioration in fats and oils transmits green light, because when the reactive substance is acted upon by sunlight or artificial light, it absorbs the very

rays that are eliminated by the green wrapper or filter used to enclose the commodity. (See Figure 4.)

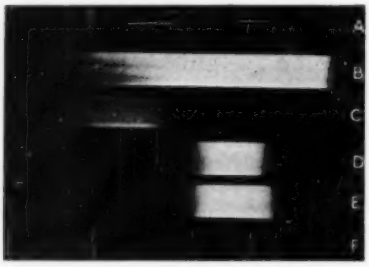

Fig. 4. Spectra of protective and nonprotective flasks.
A, F. Spectrum lines of mercury arc.
B. Spectrum of Mazda light source.
C. Transmission of blue flask.
D. Transmission of green flask.
E. Transmission of flask covered with green paper.

Commercial Importance

The importance of this whole investigation and the commercial application of its findings can be only briefly treated here. The annual food bill of this country normally exceeds 20 billion dollars. Foods valued at nearly 2 billions are, under certain conditions, subject to spoilage by rancidity. The loss due to this form of spoilage may amount to as much as 5% of the value of many of these food products.

Oxidative rancidity, so familiar to both manufacturer and consumer, is accelerated to a large extent by exposure to light both in the process of manufacture and after the products have reached the market. Foods are most subject to rancidity during the summer months, when sunlight is long and intense.

Hundreds of experiments have been conducted under intensified light conditions and also under conditions similar to those of commercial practice, both with free access of air and under vacuum, as well as under the influence of excess heat and moisture. In all cases the samples protected from light by green or black paper or foil were in appreciably better condition than those unprotected. Even those under vacuum protected by green were better than the ones in vacuum exposed freely to light. Potato chips protected from light by aluminum foil but with access to air were just as good as the chips kept in vacuum and protected by green and noticeably better than the chips kept in vacuum but exposed to light.

Some experiments have been conducted to test the protective qualities of the ordinary commercial containers in delaying rancidity and, in general, the results obtained by Arny (1931) with commercial bottles have been corroborated. Arny's work, however, was confined chiefly

to chemicals and pharmaceuticals, and as a result of his experiments he concluded that amber bottles possessed marked protective properties for pharmaceuticals. When, on the other hand, Arny used Corning color filters he found that green and red afforded the best protection.

It is known that flint glass bottles keep out much of the ultra-violet light, but according to Arny ultra-violet rays are transmitted by that kind of glass down to 3000 Ångström units. Flint glass, however, usually transmits high percentages of violet and blue light and these have been shown, in our experiments, to play an important rôle in accelerating the development of rancidity. That is one important reason why flint glass has little or no protective qualities either to delay rancidity or to prevent the fading of color.

Here at this point it may be well to call attention to Carpenter's work (1933) which has recently been published in Industrial and Engineering Chemistry. To quote his conclusions:

> In general, it appears for the present that beverage juice manufacturers marketing their products in glass containers should bear in mind the protecting influence of green on light deterioration. Some producers perhaps will not welcome green glass containers, as the clarity, color, and appeal to the eye of fruit juices are largely masked thereby. To those manufacturers the way is probably open for marketing in clear glass containers wrapped in one or another of the transparent green cellulose coverings that have recently come on the market. These coverings have the welcome feature that they are easily removed when a salesman desires to show a customer the true color of the juice without the necessity of opening the container.

Besides oil-bearing foods which are affected deleteriously by exposure to light, there are flavoring extracts, spices, essential oils, perfumes, beverages, cosmetics, and a long list of other substances that may be injuriously affected by light. Loss of potency in pharmaceuticals may be due to action of light more than the pharmacal and medical professions at present realize. One must recognize that there are numerous phases connected with light deterioration yet to be studied.

In conclusion, it must be stated that our investigation on the effect of light on oil-bearing foods has been covered only in a general way. There is much work to be done to learn what compound or compounds in oils and fats are responsible for the condition recognized as rancidity, which gives rise to these compounds, and how their formation may be prevented. After this has been accomplished there is still a vast field for investigation before us.

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CHART FOR CORRECTING CRUDE PROTEIN TO A 13.5% MOISTURE BASIS [1]

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In this laboratory several thousand Kjeldahl determinations are made annually in connection with a protein survey of the wheat crop of Western Canada, the results being expressed on a 13.5% moisture basis. Originally, the tables prepared by Shollenberger and Coleman [2] were employed for correcting the protein data to this constant moisture basis, but their use proved to be somewhat tedious due to the constant turning of pages. While one engaged in this work soon becomes familiar with the proper corrections to apply in the instance of samples falling within the normal range in crude protein and moisture content, a convenient check is required. For this purpose and also to facilitate the conversion of protein data beyond the usual ranges encountered, a chart showing the correction values has been prepared. This chart, reproduced in Figure 1, gives the necessary corrections for protein values ranging from 8.0% to 19.0% between the moisture limits of 8.0% to 17.0%. The correction to be applied in any instance is shown in the area where the protein and moisture percentages intersect. For convenience, the even corrections only have been entered on the chart.

Correction values for ranges in protein and moisture content beyond the limits shown in the chart may be computed from the following for-

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[1] Issued as Technical Paper No. 3, Grain Research Laboratory, Board of Grain Commissioners for Canada.

[2] Shollenberger, J. H., and Coleman, D. A. 1924. Tables for correcting crude protein and ash content to a uniform moisture base. U. S. Dept. Agr. Misc. Circ. 28.

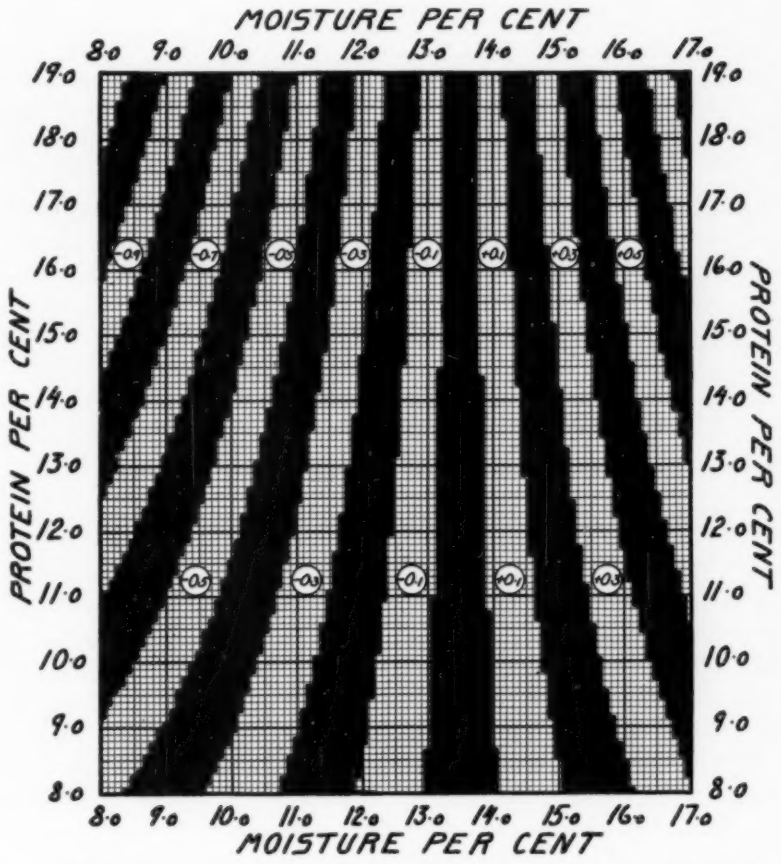

Fig. 1. Chart showing correction values for correcting crude protein to a 13.5% moisture basis.

mula:

$$\text{Correction value} = P - \frac{86.5P}{100.0 - M'}$$

where P is the uncorrected protein content at $M\%$ moisture.

A similar chart can be prepared for correcting to a 15% moisture basis by substituting the factor 85.0 for 86.5 in the numerator of the above formula.

THE INFLUENCE OF MALT, SUCROSE, AND FLOUR PROTEIN UPON THE FERMENTATION TOLERANCE OF DOUGHS TREATED WITH VARYING INCREMENTS OF POTASSIUM BROMATE

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Introduction

Various workers have discussed the changes in baking strength induced by variations in the fermentation time of the dough. In commercial practice it is usually deemed desirable to control closely the length of time the dough is allowed to ferment in the troughs. A time schedule is commonly posted at a conspicuous spot in the dough room, setting forth the correct times for "taking" each dough. A flour which allows a certain amount of "leeway" in regard to the length of time in the trough and still produces a satisfactory loaf, is looked upon by the practical baker as very desirable. In case of any alteration of the dough schedules made necessary by an emergency arising in the shop, the doughs may be required to undergo additional fermentation, and a flour or baking formula capable of conferring upon the dough the property of baking into desirable loaves under these conditions would eliminate the loss of a large number of loaves. Hence, the importance to the baking chemist, and through him to the miller, of fermentation tolerance—the range in the time of fermentation under which a flour will make good bread.

Harrel (1926) found that the fermentation times of sponge and straight doughs could be varied only slightly if desirable bread was to be produced. Similar conclusions were reached by Bailey and Johnson (1924), and St. John and Hatch (1931), who reported that the fermentation range could not exceed 50 to 80 minutes on the flour used by them. Moen (1930) concluded that the 3-hour standard basic method gave valuable information regarding the fermentation possibilities of a flour. This worker considered the question more from the standpoint of diastatic activity and its influence upon baking strength during variations in fermentation time.

The various factors affecting fermentation tolerance, as diastatic activity of the flour itself, rate of gas production and gas retention, gluten quality and quantity, etc., have been discussed at length in the literature and will not be taken up here. Bailey (1925) correlated diastatic activity with loaf volume and color, while Working (1929) stressed the utility of separating the factors of fermentation tolerance into those affecting the rate of gas production and dough rise, with consequent oven spring. The importance of an adequate supply of fermentable carbohydrate was pointed out by Swanson and Kroeker (1932) and by Jørgensen (1931). Harris (1932) mentioned the importance of sufficient yeast fermentable material in the dough when baking flours with an abnormally high percentage of yeast in the formula. These studies were conducted chiefly without potassium bromate in the baking formula.

Alcock [1] studied three millstream flours with reference to their fermentation tolerance to malt and bromate. The results indicated that increments of potassium bromate progressively decreased the fermentation tolerance, provided that the quantity of fermentable sugar was kept adequate for the demands of the yeast in the doughs. Fermentation times of 2 to 10 hours inclusive were used in this investigation.

The following baking tests were conducted by the author to obtain further data regarding the fermentation tolerance of different types of flour as influenced by various concentrations of fermentable carbohydrate and potassium bromate.

Material and Methods

A set of four flours, embracing three types of commercial flours and a composite flour milled in a laboratory mill, was used as experimental material. The crude protein, ash, and diastatic activity of these flours are shown in Table I.

TABLE I

CRUDE PROTEIN, ASH, AND DIASTATIC ACTIVITY OF THE FLOURS

Flour number	Description	Protein [1]	Ash [1]	Rumsey Units [2]
		P. ct.	*P. ct.*	
1	Composite experimentally milled straight 1932 Marquis	13.1	0.43	89
2	First patent	11.8	.36	120
3	Second patent	13.9	.46	110
4	Clear	17.8	.76	94

[1] 13.5% moisture basis.

[2] Milligrams of maltose produced by 10 gms. of flour in one hour at 30° C.

[1] See, Geddes, W. F., and Larmour, R. K. Some aspects of the bromate baking test. Cereal Chem. **10**: 55.

The baking technique employed in this work, except for the variations in fermentation time, was essentially the same as that used and fully described by the writer in former experiments in baking studies (Harris, 1932a) and will accordingly not be discussed in detail here. Bromate was used in increments of 1 to 4 mgs. and the fermentation time varied from 2 to 5 hours inclusive.

The bakings were classed in series according to the dosage of fermentable sugars incorporated in the dough. Thus Series I comprised doughs made with the basic ingredients plus 0.25% of diastatic malt, while in Series II, 2.5% of sucrose was used without malt, and in Series III both malt and sucrose were absent.

The scoring was done against a standard first patent loaf baked by the basic method with 3 hours fermentation. The values assigned this loaf were—*Color of crumb*, 20; *Grain of loaf*, 10; *Texture of loaf*, 10. In the case of the clear flour, the loaves were checked against a loaf baked from the clear by the basic 3-hour formula. This loaf was assigned a value for each quality factor by comparison with the standard patent loaf. The loaves were examined the following morning after baking.

A baking score which included loaf volume, color, and grain and texture of loaf was calculated for these loaves in the following manner:

Loaf volume cc.	$\times 0.1$
Color of crumb score	$\times 1.0$
Grain of loaf score	$\times 1.0$
Texture of loaf score	$\times 1.0$

The sum of these individual scores was considered to be the baking score of the flour.

Discussion of Results

In Table II are shown the loaf volumes and scores assigned the loaves baked in Series I.

The results obtained from baking flour No. 1 show a trend toward lower volumes and scores with the higher bromate concentrations as the fermentation period was lengthened. The same effect is noticeable for flour No. 2, where the highest loaf volumes and baking scores were produced with 2 hours fermentation. Flour No. 3, however, stood up better to longer fermentation, the volumes and scores not decreasing until 5 hours in the crock. Crumb color increased fairly regularly starting with the 2-hour bakings, and was superior in some instances to the standard first patent loaf produced by the basic formula. Optimum results for this flour were obtained with a 3-hour fermentation. The bromate dosage required to bring out the full baking strength of the flour appeared to be 2 to 3 mgs. A similar flour tested by the au-

TABLE II

LOAF VOLUMES AND BAKING SCORES ASSIGNED LOAVES BAKED WITH 0.25% DIASTATIC MALT ADDED TO THE BASIC FORMULA PLUS INCREMENTS OF BROMATE. (SERIES I)

Flour number	Fermentation time	Bromate	Loaf volume	Score			Baking score
				Color	Grain	Texture	
	Hrs.	*Mgs.*	*Cc.*				
1	2	0	465	14.5	6	5	71
1	2	1	522	16	7	6	81
1	2	2	532	17	6	6	82
1	2	3	544	17	6	5.5	83
1	2	4	565	17	6	6	85
1	3	0	510	15	7	7	80
1	3	1	522	15.5	7	6.5	81
1	3	2	527	16	6.5	6.5	82
1	3	3	545	16.5	6	6	83
1	3	4	483	16.5	6	6.5	77
1	4	0	483	15	7	7	77
1	4	1	545	16.5	7	7.5	85
1	4	2	514	16.5	7.5	7	82
1	4	3	512	16.5	6	6	80
1	4	4	445	17	5	4	70
1	5	0	465	15	6	6	73
1	5	1	532	16	7	6.5	83
1	5	2	522	14.5	5.5	5	77
1	5	3	475	14	4	5	70
1	5	4	472	13	3	5	68
2	2	0	558	21	10	10	97
2	2	1	570	22	9	9	97
2	2	2	545	21	9	8.5	93
2	2	3	550	21.5	9	8.5	94
2	2	4	552	20.5	10	9	95
2	3	0	520	19.5	9	9	89
2	3	1	526	20	8	8	89
2	3	2	555	20.5	7	7	90
2	3	3	532	20.5	7	7	88
2	3	4	512	19	7	6	83
2	4	0	511	20.5	8	8	88
2	4	1	522	20.5	9	9	91
2	4	2	518	21.5	8	8	89
2	4	3	500	21.5	6	6	83
2	4	4	472	22.5	6	5.5	81
2	5	0	480	18	7	7.5	80
2	5	1	490	19.5	10	9	87
2	5	2	478	19	9.5	8.5	85
2	5	3	435	17	7	7	74
2	5	4	447	16	5	5.5	71
3	2	0	558	17.5	7	7	87
3	2	1	590	17.5	7	7	90
3	2	2	570	17.5	7	7	88
3	2	3	590	17.5	7	7	90
3	2	4	588	18.5	8	8	93

TABLE II—(*Continued*)

Flour number	Fermentation time	Bromate	Loaf volume	Score			Baking score
				Color	Grain	Texture	
	Hrs.	*Mgs.*	*Cc.*				
3	3	0	560	19	8	8.5	91
3	3	1	650	19	7	7	98
3	3	2	672	20.5	7	7	102
3	3	3	660	20	8	7	101
3	3	4	610	19.5	7	6.5	94
3	4	0	540	18.5	8	7	87
3	4	1	604	19	9	8	96
3	4	2	665	20	7	8	101
3	4	3	680	21	7	7	103
3	4	4	594	20	6	6	91
3	5	0	508	19	7.5	7.5	85
3	5	1	632	21	6	7	97
3	5	2	640	21.5	6	6.5	98
3	5	3	615	21.5	6	6.5	95
3	5	4	555	17	4	4.5	81
4	2	0	530	8.5	4	5	70
4	2	1	582	9	6	6.5	81
4	2	2	590	9.5	6	6.5	81
4	2	3	630	9.5	5	6	83
4	2	4	620	9	5	6	82
4	3	0	540	9	4	4	71
4	3	1	618	9	8	8	87
4	3	2	664	9.5	8	8	92
4	3	3	748	10	8.5	8	101
4	3	4	750	9.5	7	6	97
4	4	0	565	8	5	5	74
4	4	1	650	8.5	8	7	88
4	4	2	752	9.5	7	7	99
4	4	3	785	10	6	6	100
4	4	4	825	10	5.5	5	103
4	5	0	538	8	6	6	74
4	5	1	618	9	7	6.5	84
4	5	2	790	9	5	5	98
4	5	3	840	9.5	4	4	101
4	5	4	850	9	3	3	100

thor, and previously reported, gave maximum results with 3 mgs. of bromate and a fermentation period of 3 hours. The high protein, low quality, clear flour data show a tendency for higher volumes and scores as the fermentation time and bromate increments were stepped up. The loaf volumes were still increasing at the 5-hour period, but the scores show a slightly lower trend, due chiefly to a decrease in grain and texture scores. Color did not exhibit any significant changes.

This series of bakings shows that the higher protein flours tend to have a greater fermentation tolerance in the presence of bromate, as well

TABLE III

LOAF VOLUMES AND BAKING SCORES ASSIGNED LOAVES BAKED WITH THE BASIC FORMULA PLUS INCREMENTS OF BROMATE. (SERIES II)

Flour number	Fermentation time	Bromate	Loaf volume	Score			Baking score
				Color	Grain	Texture	
	Hrs.	*Mgs.*	*Cc.*				
1	2	0	420		Scores not recorded		
1	2	1	440		" " "		
1	2	3	445		" " "		
1	3	0	446		" " "		
1	3	1	455		" " "		
1	3	2	460		" " "		
1	3	3	460		" " "		
1	3	4	460		" " "		
2	2	0	500	19.5	8	8	85
2	2	1	530	20.5	6	7	86
2	2	2	532	20.5	7	7	88
2	2	3	510	20	8	7.5	86
2	2	4	504	19.5	7	7	84
2	3	0	510	20	9	10	90
2	3	1	520	21	11	9	93
2	3	2	530	20	10.5	9	92
2	3	3	502	19	10.5	9	89
2	3	4	460	20.5	8	8	82
2	4	0	485	20	9	9.5	87
2	4	1	500	21	10	9.5	90
2	4	2	525	22	8	8	90
2	4	3	498	20.5	7	7	84
2	4	4	450	20.5	9	7	81
2	5	0	455	19.5	9.5	10	84
2	5	1	490	19.5	10	9	87
2	5	2	452	19	9.5	8.5	82
2	5	3	430	17	7	7	74
2	5	4	412	17	7	6	71
3	2	0	512	17.5	7	7	83
3	2	1	518	18.5	5	7	82
3	2	2	522	19	6	7	84
3	2	3	528	19	6	7	85
3	2	4	530	18.5	6.5	7.5	85
3	3	0	555	18	8	8	89
3	3	1	580	19	7	8	92
3	3	2	614	19.5	7	7	95
3	3	3	640	20	5	7	96
3	3	4	566	19.5	5	6	87
3	4	0	540	18	8	9	89
3	4	1	587	19.5	9	8.5	96
3	4	2	641	19.5	9	8	101
3	4	3	621	20	7	7	96
3	4	4	548	18	6	6.5	85

TABLE III—(*Continued*)

Flour number	Fermentation time	Bromate	Loaf volume	Score			Baking score
				Color	Grain	Texture	
	Hrs.	*Mgs.*	*Cc.*				
3	5	0	456	18	9	9	82
3	5	1	580	19	9	8	94
3	5	2	622	20	7	7	96
3	5	3	522	19	7	6	84
3	5	4	508	17.5	4	4.5	77
4	2	0	508	8.5	5	4	67
4	2	1	530	9	5	5	72
4	2	2	580	10.5	5.5	5	79
4	2	3	575	11	5	5	78
4	2	4	612	11	5	5.5	83
4	3	0	525	9	4	4	69
4	3	1	628	11	5	5	84
4	3	2	618				
4	3	3	724	12	4.5	4.5	93
4	3	4	710				
4	4	0	520	9	4	4	69
4	4	1	560	11	5	5	77
4	4	2	660	12	5	6	89
4	4	3	752	12	4.5	6	98
4	4	4	745	13	4	5	96
4	5	0	400	8	4	3	55
4	5	1	510	9.5	4	3	67
4	5	2	638	10	5	4	83
4	5	3	720	10.5	4.5	4	92
4	5	4	685	11.5	4.5	4	88

as higher bromate tolerance. Heavier bromate treatments tended to reduce the fermentation tolerance of the doughs as compared with lower dosages. This result was not apparent in the bakings with flour No. 4, probably because the fermentation period of 5 hours was not sufficiently long to show this effect of bromate.

In Table III are shown the loaf volumes and baking scores assigned the loaves baked in Series II. These loaves were baked without malt in the formula, a circumstance which threw a heavier strain on the gas producing power of the flour as the fermentation time was lengthened. Some of these doughs were doubtless suffering from yeast starvation. The data obtained from the experimentally milled flour, No. 1, was omitted after the 3-hour fermentation as no differentiation in loaf volume was shown when the doughs were treated with varying increments of bromate. This behavior can likely be ascribed to lack of gassing power, as this sample was low in diastatic activity—a characteristic of experimentally milled flours, as pointed out by Blish and Sandstedt (1927).

The results given by the other three flours are very similar to the corresponding values noted in Series I, although higher loaf volumes and scores were yielded by flours Nos. 3 and 4 when baked with malt. The optimum results, however, for each flour were obtained with the same length of fermentation for each flour in both series, 3 hours for flour No. 3 and 4 hours for flour No. 4.

TABLE IV

LOAF VOLUMES AND BAKING SCORES ASSIGNED LOAVES BAKED WITH THE BASIC FORMULA WITHOUT SUCROSE PLUS INCREMENTS OF BROMATE. (SERIES III)

Flour number	Fermentation time	Bromate	Loaf volume	Scores			Baking score
				Color	Grain	Texture	
	Hrs.	*Mgs.*	*Cc.*				
2	2	0	512		Scores not recorded		
2	2	2	478		" "	"	
2	2	4	510		" "	"	
2	3	0	502	19.5	7	7	84
2	3	2	505	20	8	7	86
2	3	4	458	20.5	8	7.5	82
2	4	0	430	19	4	4	70
2	4	2	488	18	4	4	75
2	4	4	400	18	2	3	63
3	2	0	516	17	6	5	80
3	2	2	530	18	6.5	7	84
3	2	4	590	18.5	6	7.5	91
3	3	0	488	15.5	5.5	6	76
3	3	2	560	16	7	7.5	86
3	3	4	580	16	6	7	87
3	4	0	364	15	5	5	61
3	4	2	460	16	6	6	74
3	4	4	505	16.5	5	5	77
4	2	0	522	7.5	4	4	68
4	2	2	585	8.5	4	4	68
4	2	4	618	9.5	6.5	5	82
4	3	0	398	8	5	4.5	57
4	3	2	504	9	5.5	5	70
4	3	4	634	9	4.5	4	81
4	4	0	342	8	4	4	50
4	4	2	490	8	3.5	3	63
4	4	4	530	7.5	3	3	66

In Table IV are shown the loaf volumes and scores assigned the loaves baked in Series III. These loaves were baked without either malt or sucrose in the formula, and therefore the only source of fermentable sugars was contained in the flour itself. Flour No. 1 was again left out of this series.

The effect of lack of gassing power is quite clearly shown in this series of tests. The control doughs show progressive decreases in loaf volumes and baking scores as the fermentation is lengthened, the clear flour, No. 4, being the most affected, and No. 2, the first patent flour, the least affected. When the bromated loaves data are examined, an improvement is noted in every instance but one over the corresponding controls. The bromate in this instance appears to increase the fermentation tolerance in the absence of added fermentable sugars. This improvement tends to become more marked with increasing protein of the flour and concentration of bromate. Only 2 bromate increments, 2 and 4 mgs., were used in this series on account of flour shortage, and the maximum fermentation period was limited to 4 hours.

In previous studies by the author (Harris, 1932a) the effect of high levels of diastatic malt was investigated, dosages of 2%, 4% and 6% being used. It was found that the 2% and 4% treatments had a beneficial action, while 6% of malt reacted favorably with the high protein flours, but decreased the loaf volumes of the lower protein flours. Ac-

TABLE V

LOAF VOLUMES GIVEN BY FLOURS BAKED WITH 4% DIASTATIC MALT AND 2 AND 4 MGS. BROMATE. (SERIES IV)

Flour number	Fermentation time	Bromate	Loaf volume
	Hrs.	*Mgs.*	*Cc.*
1	3	0	560
	3	2	542
	3	4	512
	5	0	522
	5	2	465
	5	4	440
2	3	0	540
	3	2	568
	3	4	512
	5	0	540
	5	2	498
	5	4	422
3	3	0	580
	3	2	610
	3	4	608
	5	0	625
	5	2	580
	5	4	520
4	3	0	620
	3	2	680
	3	4	715
	5	0	608
	5	2	750
	5	4	730

cordingly, in the present instance, a further series, No. 4, of bakings was conducted using the malt level of 4% to ascertain the effect of additions of potassium bromate upon fermentation tolerance at a relatively high malt level. The increments of bromate employed were 2 and 4 mgs., and the fermentation times were 3 and 5 hours only. No baking scores were computed for these loaves on account of the darkening of the crumb caused by the high malt concentration. The loaf volumes are shown in Table V.

Loaf Volumes

The loaf volumes obtained by using the various baking methods are shown in Table VI without the bread scores to facilitate comparison.

Examining the results of Series I, it will be seen that flours No. 1 and 2 gave their highest loaf volume when baked by the 2-hour fermentation period, while flour No. 3 yielded the best loaf at the 3-hour period and flour No. 4 at the 5-hour period. From this it would appear that the higher the flour protein the longer the fermentation required to obtain the maximum loaf volume. The stronger commercial flours also tended to show greater fermentation tolerance in the presence of 0.25% of diastatic malt.

In Series II the limiting effect of lowered gas production is evident as the fermentation time is lengthened. Flour No. 4, in particular, is adversely affected, although all the flours show lower volumes for each bromate increment in the 5-hour period. Flour No. 2 is adversely affected by 4 mgs. of bromate when fermented 2 hours, and by 3 mgs. when fermented 3 hours. Flour No. 3 weakened at 3 hours when treated with 4 mgs. of bromate, and at 5 hours in the presence of 3 mgs. of bromate; while the same trend is noticeable for flour No. 4 at the 5-hour fermentation period. In view of these results it seems that the tolerance to longer fermentation of this series of doughs was lowered by heavier dosages of bromate. Again, the fermentation time required to produce the largest loaf appears to be directly related to flour protein.

The results of Series III show the effect of yeast starvation as fermentation progressed. The 2-hour loaves do not differ markedly from the corresponding values for Series II, but when fermented for 3 hours the doughs show the effect of lack of fermentable sugar with consequent lower volumes for the controls of flours 3 and 4, and the 2 mgs. of bromate dough of flour No. 4. The loaves containing 4 mgs. of bromate show no appreciable decrease for these two flours, while the corresponding loaf for flour No. 2 is much poorer. This difference in behavior may probably be attributed to the lower protein content of the latter flour. When fermented for 4 hours all the flours yield smaller loaves than the corresponding loaves when fermented for 3 hours. Increments

TABLE VI

LOAF VOLUMES OBTAINED FROM THE FOUR FLOURS USING THE VARIOUS BAKING METHODS

Baking formula	Fermentation time	Loaf volumes of flours				
		No. 1	No. 2	No. 3	No. 4	Mean
	Hrs.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
0.25% diastatic malt	2	465	558	558	530	528
0.25% diastatic malt + 1 mg. of bromate	2	522	570	590	582	566
0.25% diastatic malt + 2 mgs. of bromate	2	532	545	570	590	559
0.25% diastatic malt + 3 mgs. of bromate	2	544	550	590	630	578
0.25% diastatic malt + 4 mgs. of bromate	2	565	552	588	620	581
	Mean	526	555	579	590	562
0.25% diastatic malt	3	510	520	560	540	532
0.25% diastatic malt + 1 mg. of bromate	3	522	526	650	618	579
0.25% diastatic malt + 2 mgs. of bromate	3	527	555	672	664	604
0.25% diastatic malt + 3 mgs. of bromate	3	545	532	660	748	621
0.25% diastatic malt + 4 mgs. of bromate	3	483	512	610	750	589
	Mean	517	529	630	664	585
0.25% diastatic malt	4	483	511	540	565	525
0.25% diastatic malt + 1 mg. of bromate	4	545	522	604	650	580
0.25% diastatic malt + 2 mgs. of bromate	4	514	518	665	752	612
0.25% diastatic malt + 3 mgs. of bromate	4	512	500	680	785	619
0.25% diastatic malt + 4 mgs. of bromate	4	445	472	594	825	584
	Mean	500	505	617	716	584
0.25% diastatic malt	5	465	480	508	538	498
0.25% diastatic malt + 1 mg. of bromate	5	532	490	632	618	568
0.25% diastatic malt + 2 mgs. of bromate	5	522	478	640	790	608
0.25% diastatic malt + 3 mgs. of bromate	5	475	435	615	840	591
0.25% diastatic malt + 4 mgs. of bromate	5	472	447	555	850	581
	Mean	493	466	590	727	569
Basic formula	2	410	500	512	508	507
Basic formula + 1 mg. of bromate	2	430	530	518	530	526
Basic formula + 2 mgs. of bromate	2	—	532	522	580	545
Basic formula + 3 mgs. of bromate	2	435	510	528	575	538
Basic formula + 4 mgs. of bromate	2	—	504	530	612	549
	Mean		515	522	561	533
Basic formula	3	435	510	555	525	527
Basic formula + 1 mg. of bromate	3	445	520	580	628	576
Basic formula + 2 mgs. of bromate	3	450	530	614	618	587
Basic formula + 3 mgs. of bromate	3	450	502	640	724	622
Basic formula + 4 mgs. of bromate	3	450	460	566	710	579
	Mean	446	504	591	641	578
Basic formula	4		485	540	520	515
Basic formula + 1 mg. of bromate	4		500	587	560	549
Basic formula + 2 mgs. of bromate	4		525	641	660	609
Basic formula + 3 mgs. of bromate	4		498	621	752	624
Basic formula + 4 mgs. of bromate	4		450	548	745	581
	Mean		492	587	647	576

TABLE VI—(*Continued*)

Baking formula	Fermentation time	Loaf volumes of flours				
		No. 1	No. 2	No. 3	No. 4	Mean
	Hrs.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
Basic formula	5		455	456	400	437
Basic formula + 1 mg. of bromate	5		490	580	510	527
Basic formula + 2 mgs. of bromate	5		452	622	638	571
Basic formula + 3 mgs. of bromate	5		430	522	720	557
Basic formula + 4 mgs. of bromate	5		412	508	685	535
	Mean		448	537	591	525
Basic formula without sucrose	2		512	516	522	517
Basic formula without sucrose + 2 mgs. of bromate	2		478	530	585	531
Basic formula without sucrose + 4 mgs. of bromate	2		510	590	618	573
	Mean		497	545	575	540
Basic formula without sucrose	3		502	488	398	463
Basic formula without sucrose + 2 mgs. of bromate	3		505	560	504	523
Basic formula without sucrose + 4 mgs. of bromate	3		458	580	634	557
	Mean		488	543	512	514
Basic formula without sucrose	4		430	364	342	379
Basic formula without sucrose + 2 mgs. of bromate	4		488	460	490	479
Basic formula without sucrose + 4 mgs. of bromate	4		400	505	530	478
	Mean		439	443	454	445
4% diastatic malt	3	560	540	580	620	575
4% diastatic malt + 2 mgs. of bromate	3	542	568	610	680	600
4% diastatic malt + 4 mgs. of bromate	3	512	512	608	715	587
	Mean	538	540	599	672	587
4% diastatic malt	5	522	540	625	608	574
4% diastatic malt + 2 mgs. of bromate	5	465	498	580	750	573
4% diastatic malt + 4 mgs. of bromate	5	440	422	520	730	528
	Mean	476	487	575	696	558

of 4 mgs. of bromate produced the smallest loaf for flour No. 2, and the largest for flours 3 and 4 when fermented for 3 hours. In the absence of sucrose or other added fermentable sugar, bromate seems to increase fermentation tolerance over the time range studied, at least on the higher protein flours.

In the series baked with 4% diastatic malt in the formula, potassium bromate appeared to have a marked detrimental effect upon the loaf volumes of the three weaker flours when the doughs were fermented for 5 hours. This is in line with the work of Alcock.[2] At this fermentation time flour No. 4 still showed increased volume for the bromated loaves, as compared with the 3-hour results. When compared

[2] See footnote 1, page 261.

with Series I, which contained 0.25% malt, the control loaves are larger in every instance in the presence of 4% malt. This relationship can be noted between the 2 and 4 mg. of bromate levels for the 3-hour fermentation, but when the fermentation was extended to 5 hours, the doughs containing 4% of malt tended to give smaller loaves. The response to this malt level at the usual fermentation time of 3 hours was directly

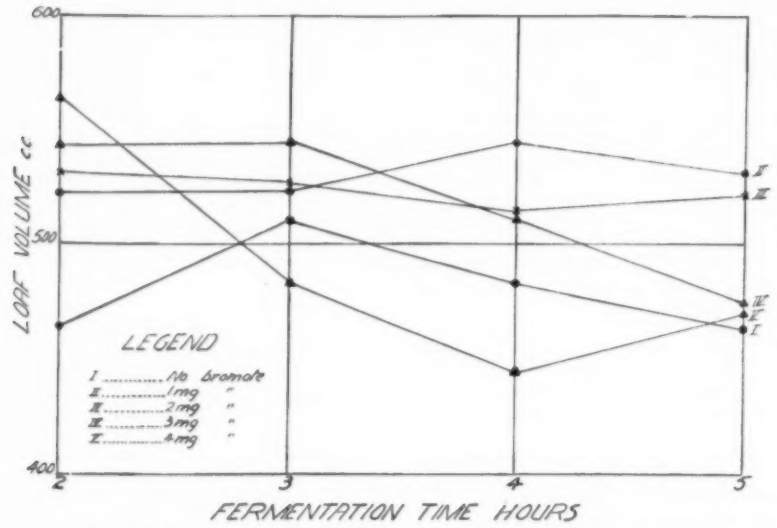

Fig. 1. Composite experimental flour baked by basic formula plus 0.25% of diastatic malt.

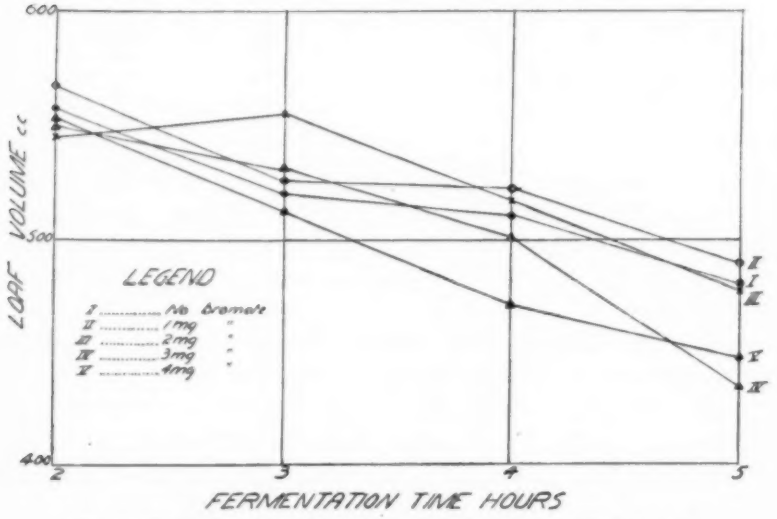

Fig. 2. Patent flour baked by basic formula plus 0.25% of diastatic malt.

related to the protein content of the flours, and agrees with previous findings of the author.

Discussion of Graphs

Figures 1 to 4 inclusive represent graphically the data for the Series I bakings with 0.25% of malt in the formula. Figures 1 and 2 are very similar, 1 mg. of bromate increasing the loaf volume throughout the 5 hours. The 2 mgs. increment of bromate is next in order of effectiveness, while the 3 and 4 mg. dosages decrease in tolerance in the order named. Bromate increased the fermentation tolerance of flour No. 3, this effect reaching its maximum with 2 mgs., then decreasing through 3 to 4 mgs., but does not reach the zero bromate value at 5 hours. For

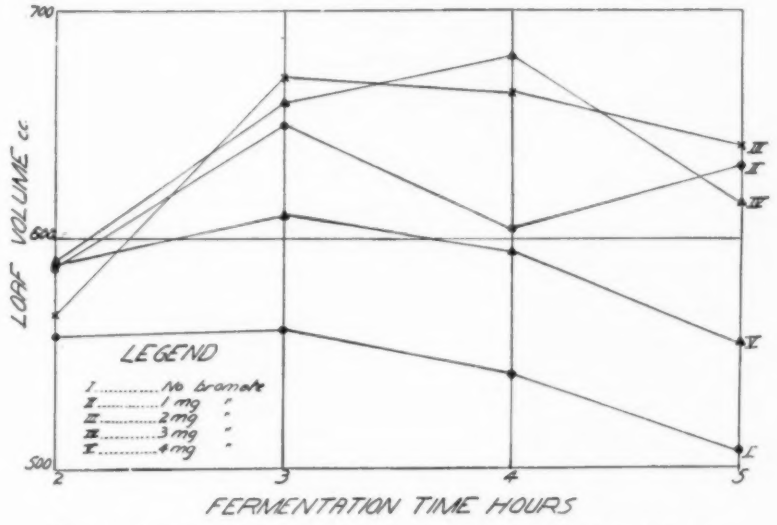

Fig. 3. Bakers' patent flour baked by basic formula plus 0.25% of diastatic malt.

flour No. 4 a progressive increase in tolerance is evident with each increment of bromate.

Mean Loaf Volumes

The mean loaf volumes of the various flours when baked by the different methods are shown for both controls and bromated loaves in Table VII. The mean loaf volume for each individual flour in each series is shown in Table VIII, with the mean loaf volume yielded by each flour when baked by all the methods, as well as the mean loaf volumes for each series, arranged according to bromate dosage. The final mean value for each increment of bromate in the series is also shown.

From the results given in Table VII, the effect of flour protein upon fermentation tolerance is evident. The first 3 series show a trend toward maximum loaf volume with longer fermentation as the fermentable carbohydrate is increased. Yeast starvation in Series III causes a quick reduction in loaf volume as the fermentation period is lengthened.

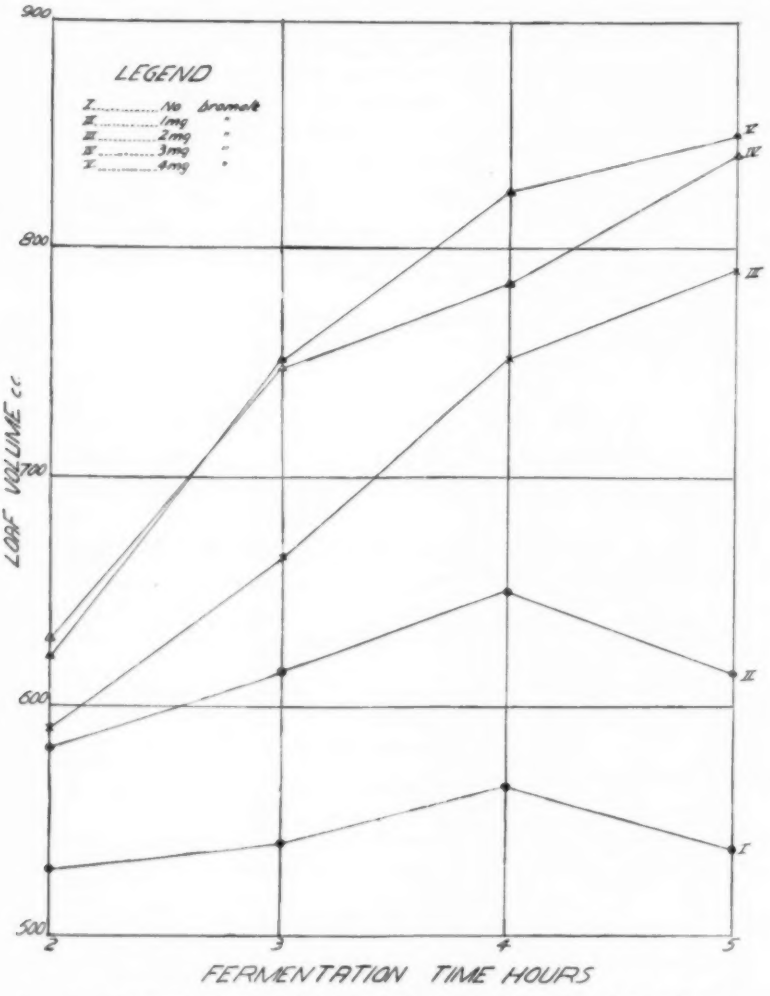

Fig. 4. High protein clear flour baked by basic formula plus 0.25% of diastatic malt.

Table VIII reveals an increase in the mean loaf volume of the various flours as the protein increases, regardless of the type of the flour. The bakings with 0.25% and 4% of diastatic malt yield almost identical results, but it must be borne in mind that the 4% malt bakings were

TABLE VII

MEAN LOAF VOLUMES OF THE FLOURS WHEN BAKED WITH DIFFERENT FERMENTATION PERIODS

Fermentation period	Flour number			
	1	2	3	4
Hrs.	*Cc.*	*Cc.*	*Cc.*	*Cc.*
		Series I. 0.25% malt in formula		
2	526	555	579	590
3	517	529	630	664
4	500	505	617	716
5	493	466	590	727
		Series II. Basic formula		
2		515	522	561
3		504	591	641
4		492	587	647
5		448	537	591
		Series III. No sucrose in formula		
2		497	545	575
3		488	543	512
4		439	443	454
		Series IV. 4% malt in formula		
3	538	540	599	672
5	476	487	575	696

only conducted at two fermentation periods, 3 and 5 hours. This fact would probably tend to lower the mean, the lower values were usually yielded by three of the flours at the longer fermentation. The bakings without malt gave smaller loaves, while in the absence of sucrose in addition to malt, the results were the lowest of all, indicating the importance of a suitable supply of fermentable sugars.

This table also shows a trend toward increasing volumes with increasing bromate increments. The maximum response appears to be reached with 3 mgs., the next increment, 4 mgs., causing a reduction

TABLE VIII

MEAN LOAF VOLUMES ARRANGED ACCORDING TO FLOUR NUMBER AND BROMATE INCREMENTS

Series	Flour number					Bromate increments—*Mgs.*				
	1	2	3	4	Mean	0	1	2	3	4
	Cc.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
I	518	514	604	674	577	521	573	596	602	584
II		490	559	610	553	496	544	578	585	561
III		475	510	514	500	453		511		536
IV	507	513	587	684	573	574		586		557
Means	512	498	565	627		511	558	573	593	559

in loaf volume. In Series III, the 3-mg. treatment is missing, so it cannot be definitely stated that the final 4-mg. bromate treatment lowered the volume. Judging from the results in this table, 3 mgs. of bromate would be the correct dosage required to bring out maximum strength in a series of bakings which included various fermentation periods and malt levels.

Although it was found that 1 mg. of bromate caused a general improvement in fermentation tolerance, 3 and 4 mg. dosages, while affecting favorably the stronger flours, decreased the tolerance for the low protein flours. It seemed probable from these results when taken in conjunction with Alcock's work that bromate would reduce the fermentation tolerance of all flours provided that the fermentation period was lengthened sufficiently and the supply of fermentable sugars was kept high enough to prevent yeast starvation becoming marked in the longer time doughs. In order to throw more light on this question, a further set of bakings was conducted using a more extensive range in fermentation time than had been employed in the bakings already described.

Two commercial flours, differing by 3% of crude protein, were used for this study. One sample was flour No. 2 described in Table I, and the other was a straight grade flour, No. 5, containing 14.8% protein and 0.49% ash (13.5% moisture basis). The diastatic activity in Rumsey units was 132. The fermentation periods employed were 0, 1, 2, 5 and 7 hours. The baking formulas consisted of the standard basic, with additions of 0.25%, 1% and 4% diastatic malt. Bromate was used in increments of 2 and 4 mgs. No baking scores were computed for these loaves as the loaf scores were found to follow very closely the loaf volumes in the bakings previously discussed. A record was kept in the present instance of abnormal crust color, texture and loaf appearance, and these are noted when quite marked. The loaf volumes obtained in these bakings are shown in Table IX.

The data collected for flour No. 2 show a rise in loaf volume starting from the doughs without crock fermentation until the 2 to 3 hour doughs, followed by a decrease to the 7 hour loaves. The crust color of the 5 and 7 hour loaves was very pale in every instance, regardless of the presence or absence of bromate, while the crumb and texture of these loaves were also poor. The doughs which were panned immediately after mixing produced small, poorly shaped loaves of very close texture. The 1-hour doughs baked into much better loaves, while the 2-hour loaves were quite normal in every respect. The addition of 2 mgs. of bromate did not materially affect the loaf volumes, but a dosage of 4 mgs. caused a breakdown at the 3-hour fermentation, followed by a

TABLE IX

LOAF VOLUME OF THE FLOURS TREATED WITH VARIOUS INCREMENTS OF POTASSIUM BROMATE

Fermentation time	Basic formula plus increments of $KBrO_3$—*Mgs.*			Malt formula[1] plus increments of $KBrO_3$—*Mgs.*			Malt formula[2] plus increments of $KBrO_3$—*Mgs.*			Malt formula[3] plus increments of $KBrO_3$—*Mgs.*		
	0	2	4	0	2	4	0	2	4	0	2	4
Hrs.	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*	*Cc.*
						Flour No. 2						
0	350	348	—	380	372	374	—	—	—	400	—	400
1	430	420	—	476	460	465	490	—	490	520	—	492
2	500	532	504	558	545	552	560	563	510	592	545	550
3	510	530	460	520	555	512	566	510	510	555	568	512
5	455	452	412	480	478	447	528	485	430	540	498	422
7	400	390	348	475	432	413	480	420	400	496	390	350
						Flour No. 5						
0	372	—	—	382	—	390	—	—	—	—	—	—
1	480	502	502	470	—	475	490	—	498	—	—	—
2	580	590	594	570	601	580	615	—	672	652	658	656
3	600	669	667	623	644	648	630	680	662	630	623	616
5	575	635	544	568	591	549	604	600	572	636	618	545
7	485	519	470	530	550	450	600	562	475	578	490	422

[1] Basic ingredients plus 0.25% diastatic malt.
[2] Basic ingredients plus 1% diastatic malt.
[3] Basic ingredients plus 4% diastatic malt.

rapid decrease in loaf volume as the time was lengthened to 7 hours in the crock.

Flour No. 5 reacted somewhat differently. The volume of the control loaves held up fairly well to the 5-hour fermentation. The addition of 2 mgs. of bromate increased the size after 1 hour fermentation and apppeared to improve the fermentation tolerance. When 4 mgs. of bromate was added, however, the tolerance was impaired after 3 hours fermentation. The higher diastatic activity of this flour doubtless caused an improvement in fermentation tolerance as compared with flour No. 2. The crust color was slightly pale when these doughs were fermented for 7 hours, while the doughs fermented 2 hours or less were "harsh" in feeling, and produced loaves of inferior color, grain and texture.

When these flours were baked with 0.25% of malt, a general increase in loaf volume was evident for flour No. 2. The doughs containing 2 mgs. of bromate fell off after 3 hours and the 4-mg. doughs after 2 hours fermentation. The crust color was slightly pale for the 7-hour loaves. The addition of 2 mgs. of bromate increased the fermentation tolerance very slightly for No. 5, but the addition of 4 mgs. impaired this property very markedly when the doughs were fermented 7 hours. The

values for this flour were not appreciably raised above the corresponding volumes obtained without malt except for the controls in the final period. These 7 hour loaves showed a slightly pale crust.

A concentration of 1% malt somewhat delayed the decrease in loaf volume as the fermentation time was lengthened. For flour No. 1, the 1 hour results tended to be higher, especially in comparison with the values obtained without malt in the formula. The fermentation tolerance was decreased by both increments of bromate after 2 hours of fermentation. Very little decline is evident in the flour No. 5 values for the longer timed doughs baked without bromate. Addition of 2 mgs. of bromate to these doughs lowered the loaf volume after 7 hours in the crock, while 4 mgs. caused the volume to fall below the control value following 5 hours fermentation. Crust color was practically normal for all the loaves in this baking after 7 hours fermentation.

The use of 4% diastatic malt in the doughs resulted in a decided stimulation in loaf volume of the control for flour No. 2. The 1 hour loaves were larger, and the loaves baked from doughs fermented 2 hours were superior to any of the preceding loaves produced from this flour. The loaf obtained at the 7-hour period was only slightly inferior to the best control loaf baked without malt. None of the bromated loaves approach the controls in volume. The doughs containing 2 mgs. of bromate broke after 5 hours fermentation, while those treated with 4 mgs. decreased in volume after 3 hours. The volumes of the bromated loaves fermented 7 hours are identical with the corresponding non-malted values. The data for flour No. 5 show a marked reduction in fermentation with bromate, the 2-mg. doughs commencing to fail at 3 to 5 hours, and the 4-mg. doughs at 3 hours. The crust color of all loaves baked with 4% of diastatic malt in the formula was quite good after 7 hours in the crock.

Summary and Conclusions

Malt increased the fermentation tolerance of all unbromated doughs in these bakings, in proportion to the quantity added, while sucrose also increased this property in doughs lacking in malt. The experimental flour used in this study gave unsatisfactory results unless malt was included in the baking formula.

Potassium bromate at a low concentration increased the fermentation tolerance of the doughs, provided that a limit of five hours fermentation was not exceeded. Increasing the dosage of bromate tended to exert a detrimental effect upon fermentation tolerance, especially if a long fermentation period was employed.

In the absence of malt and sugar in the formula, bromate apparently increased the fermentation tolerance of four-hour doughs.

The effect of potassium bromate upon fermentation tolerance appeared to be largely conditioned by the quantity of protein present in the flour. Lower protein flours had this property impaired by more than 2 mgs. of bromate while a strong clear flour stood 4 mgs. at the end of a five hour fermentation. All flours, however, would seem to have their fermentation tolerance lowered by addition of bromate, provided that the fermentation period was sufficiently long and that a plentiful supply of fermentable sugars was available for yeast activity in the dough.

Acknowledgment

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BAKING QUALITY OF FLOUR AS AFFECTED BY CERTAIN ENZYME ACTIONS

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Introduction

The baking qualities of flours as determined by their gluten and enzymic properties are subject to wide variation from year to year as a consequence of climatic and other factors which control the chemical and physical characteristics of wheat. On the more practical side the enzymic quality has been concerned chiefly with diastatic activity.

The question of what constitutes desirable quality in gluten is not thoroughly understood. "Buckiness" (extreme toughness or lack of ductility) in doughs is attributed to certain defects of the gluten. Such doughs yield an inferior loaf of bread having a poor crumb structure, which is also frequently marred with large holes. It is recognized that faulty manipulation of the dough in the bakeshop may be responsible for some of the holes which frequently occur in bread, but the difficulties herein referred to arise from factors inherent in the baking characteristics of the flour from which the dough is prepared.

The common practice of stepping up the diastatic activity of flours by incorporating a small amount of some malt flour is beset with some danger unless carefully regulated and controlled. Recent investigations by Kozmin (1933) indicate that certain difficulties may arise from excessive starch hydrolysis rather than from other factors. There is also evidence for believing that some of the observed benefits noted in properly diastased flours may be attributed to factors apart from the added diastase. It is generally conceded by those who have studied the question, that the protease content of added malt flour plays a beneficial rôle in many instances.

The studies which are presented in this paper were undertaken to determine whether appropriate quantities of commercial preparations of proteolytic enzymes and combinations of diastatic and proteolytic ferments exert any beneficial action on the gluten of flours which normally yield "bucky" doughs.

The mellowing of the gluten of a "bucky" dough during the processes of fermentation might remove certain difficulties and enable one

to secure an excellent loaf of bread from such dough by the usual bake-shop procedure. A large number of baking tests were, therefore, made with flours of harsh gluten which tended to produce "bucky" doughs, employing both sponge and straight dough methods. Experiments were conducted with flours prepared in the laboratory from malted wheat and from malted barley, with commercially prepared proteases such as papain, pepsin, and trypsin, with commercial diastase prepared from malt (Merck's U. S. P. grade), which is high in malt protease, and with other diastatically active preparations.

Enzymes in Malt and Malt Products

Amylases

The enzymes in malt flours and other malt products which it seems advisable to consider in this connection are: (1) the starch liquefying, (2) the saccharifying, and (3) the proteolytic. Bach, Oparin, and Vener (1926) reported quantitative studies on the variation of enzymes in wheat in the course of ripening, resting, and germinating. They found that in the process of ripening the protease and amylase content very materially decreased, but during germination there occurred a phenomenal increase of protease and amylase.

Frankel and Hamburg (1907) separated diastase of malt into starch liquefying and saccharifying components by means of dialysis.

Olsen and Fine (1924) found that the optimum hydrogen-ion concentration for malt diastase, as measured at 25° C., varied from pH 4.3 to 6.0 as the temperature was raised from 25° to 69° C. They also pointed out that the liquefaction curve followed the saccharification curve closely at the higher temperatures, indicating that both processes apparently have the same optimum pH.

According to Gore and Józsa (1932) the liquefying power of diastase is not concerned directly with the attack of diastase on the raw starch of flour. Commercial flours have both liquefying and saccharifying activity. In a separate paper (1932a) they also reported that the saccharifying power of diastase appears to be much less widely distributed in plant products than the liquefying power. They also found that the activity of both these components of diastase was materially increased by additions of sodium chloride or papain.

Ohlsson (1930) pointed out that malt amylase is a mixture of two different amylases, an α-amylase (dextrinogenic), and a β-amylase (saccharogenic). The stability of the two enzymes was not dependent in the same manner upon H-ion concentration and temperature. The α-amylase was completely destroyed by bringing a malt solution at 0° to a pH of 3.3 with HCl and, after 15 minutes, changing the pH to 6.0

by the addition of Na_2HPO_4. The saccharogenic or β-amylase still retained 70% to 80% of its activity. On the other hand, the heating of a malt solution at pH 6.0 to 7.0 for 15 minutes at 70° C. completely destroyed the β-amylase while the dextrinogenic or α-amylase remained 75% active. The saccharogenic component was shown to have an activity curve with a broad optimal zone between pH 4.0 and 5.75, while the optimum for dextrinogenic amylase was found to be within a pH range of 5.5 to 6.0. In the hydrolysis of starch the main products of the α-amylase activity are dextrins, while the β-component liberates maltose from starch from the outset.

Edfeldt, Nordh, and Swaetichin (1930) reported experiments supporting Ohlsson's conclusion, that diastase of malt is composed of two amylases which can be differentiated by their reaction to temperature and hydrogen-ion concentration, and not of an amylase and dextrinase as held by certain other investigators.

Van Klinkenberg (1931) separated and studied the action of the α- and β-amylases of malt on potato starch paste. The optimum pH for the α-amylase was 4.55–5.15 and for β-amylase 5.65–5.85. The latter liberated a maximum of 64% of the theoretical amount of maltose from soluble potato starch, irrespective of the amount of enzyme used. When α-amylase acted upon soluble starch, it quickly liberated about 36% of the theoretical amount of maltose, and then slowly liberated up to about 50%. Glycogen proved a poor substrate for β-amylase, but a good one for the α-amylase. This supports the conclusion that pancreatic and fungus amylases are of the α-form, as both animals and fungi contain glycogen.

Kozmin (*loc. cit.*) has presented important and interesting data in connection with certain studies dealing with the biochemical characteristics of dough and bread made from sprouted wheat. The conclusion was reached that the absolute value of the saccharogenic power of the flour had no direct influence upon the rate of fermentation, provided that power did not fall below a certain minimum required for a given amount of yeast, without the addition of sugar.

On the contrary the dextrinizing capacity must not exceed certain limits. These limits are exceeded in flour from grain which has undergone germination, and the defectiveness of bread baked from sprouted wheat flour as compared with normal flour is caused by the excessive splitting of starch, particularly during the early stages of baking. As a result, a much higher content of water soluble substances is contained in the bread in the form of reducing sugars and dextrins, and there is not enough of starch, after gelatination in the baking process, to bind all the water in the dough. Consequently, the crumb is moist and sticky even after extended baking. The notable lack of elasticity in the crumb

is attributed to the destruction of the solid gel structure of the starch, which together with the gluten structure is responsible for the texture and grain characteristics of the crumb.

The importance of the dextrinizing or liquefying factor in the diastatic complex has been largely overlooked. When this action of the high diastatic flours from sprouted wheat was inhibited during the baking process, by having the dough at a pH of 4.5, the crumb structure was on a par with that of bread made from normal flour. It was also found that the splitting of gluten during the fermentation and baking of doughs made from malted wheat flour did not occur to the extent of becoming appreciably noticeable in the water soluble components extracted from the dough and from the bread.

Proteases

Papain and the proteolytic enzymes of malt are vegetable proteases. Papain is the name given to the proteolytic enzyme elaborated by *Carica papayo* L. (papaw), and is obtained chiefly from the green fruit. The unripe fruit is scarified and the milky juice which exudes is collected and sun dried. The resulting gum is exported. In more recent years cultivation of the papaya and production of the crude gum has received some attention in the Philippine Islands. The West Indies, Mexico, and Ceylon export the best grades of gum.

Mendel and Blood (1910) reported an extensive study concerned with some peculiarities of the proteolytic activity of papain, which is phenomenally accelerated by the presence of HCN. These authors pointed out that this activity of HCN was not to be attributed to a peculiarly favorable concentration of hydrogen-ions, nor to the destruction of some inhibiting substance either in the papain or substratum, nor to the activation of a papain zymogen. Rather the behavior of HCN should be considered comparable to the action of a co-enzyme. The acceleration phenomena induced by HCN, together with other peculiarities of the enzyme, place papain in a different category from pepsin, trypsin and animal erepsin and also in contrast with other vegetable enzymes.

Frankel (1917) pointed out that the conditions of acidity for the optimum action of papain are pH 5.0. In connection with the use of HCN as an accelerating agent Frankel found that it could be recovered almost quantitatively from a digestion mixture, thereby indicating that it was not utilized in the reaction. He also reported that papain with or without HCN, appeared to have no proteolytic effect on the dipeptides studied.

Ambros and Harteneck (1929) reported that commercial papain hydrolyzes proteins but not peptones or protamines, but when treated

with HCN it acquires the power of hydrolyzing peptones and protamines. Fresh latex obtained from the fruit contains the enzyme in the activated state, but the activator does not occur in the dried commercial preparations. The natural activating agent is not HCN. It is a kinase which they termed phyto-kinase.

They also found that pineapple protease (bromelin) was similar to papain in most respects, and state that it seems probable that all plant proteases capable of activation by HCN are one and the same enzyme,

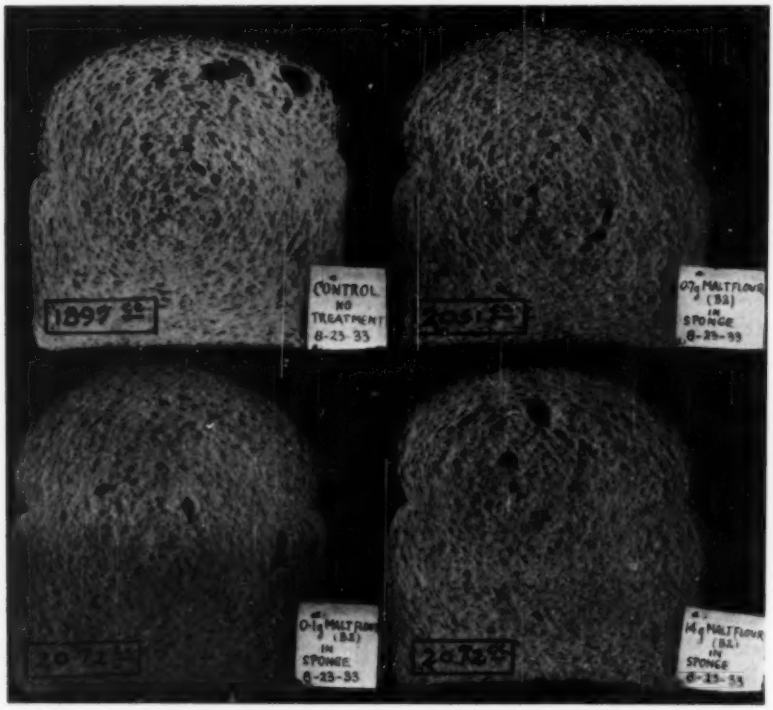

Fig. 1. Baking results with flour No. 121988, showing effects on crumb structure produced by varying quantities of barley malt flour No. II, when added to the sponge. This was a normal malt flour giving a saccharogenic index of 382 on flour sample No. 119304.

the apparent difference in specificity being due simply to variations in the amount of natural activator present. Unlike the papaw, the ripe pineapple yields the completely activated enzyme and HCN is without effect.

In a subsequent paper (1929a) the same authors reached the conclusion that the protease system of plants consists of two types of proteases. The one is a proteinase, represented by papain which is activated by HCN and the other is a dipeptidase, which is inhibited by HCN. Its

pH optimum for alanyl-glycine is 7.6 and it closely resembles the dipeptidase of yeast and animal intestine. The dipeptidase occurred in all the plants examined and in all parts of the plant except the latex.

Lüers and Malsch (1929) reported the presence of a *protease* and a *peptidase* in infusions of *green malt*. On a gelatin substrate the optimum pH was found to be 4.9 to 5.0. In the presence of HCN the activity of the protease was increased nearly 50%, the optimum pH in this

Fig. 2. Baking results with flour No. 121457, showing effects on crumb structure produced by diastase of malt when added alone to the sponge and in combination with papain.

case being 4.6 to 4.7. The peptidase acted upon leucyl-glycine at an optimum pH of 7.5. The peptidase was easily destroyed below pH 5.0. Both enzymes are sensitive to alcohol, the protease being particularly so. For the selective adsorption of both enzymes the optimum pH is 5.0. The protease is the more readily adsorbed.

Mill and Linderstrom-Lang (1929) assumed that there are at least two proteolytic enzymes in green malt. One is a protease which acts on gelatin, edestin, and egg albumin peptone. When the protease is

allowed to act on edestin at 40° C. the optimum pH is 4.3. The other protease is a peptidase which breaks up leucyl-glycine, the optimum pH for this action being 7.6–7.9 at 40° C. Phosphates greatly inhibited the action of this peptidase and the enzyme readily decomposed when the malt extract at its natural reaction (pH — 5.9) was allowed to stand at ordinary temperature.

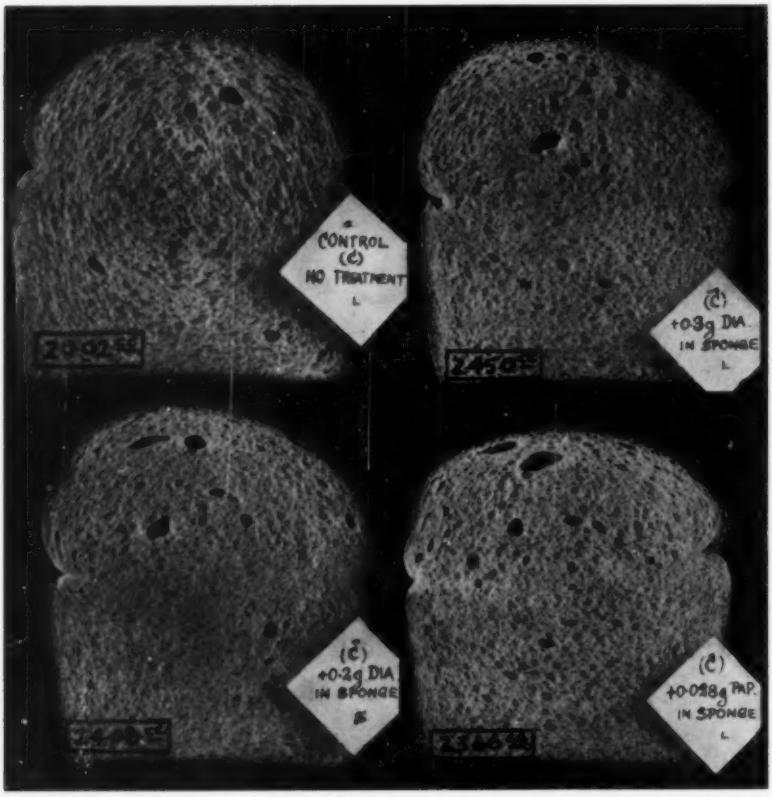

Fig. 3. Baking results with flour No. 121944, showing effects on crumb structure produced by diastase of malt and papain when added separately to the sponge. (Baked 8–7–33.)

Soon thereafter Linderstrom-Lang and Sato (1929) reported that malt extract contained a proteinase which was capable of acting upon edestin at pH 4.1, and a peptidase which would split di- or tri-peptides at pH 8.0.

Hopkins and Kelly (1931) pointed out that the proteinase of malt acts optimally at 46° C. on crystalline egg albumin at pH 3.3 to 3.6, on casein at pH 3.35 and at 5.57, on fibrin at pH 3.8 and 6.0 and at 37° C. on edestin at pH 3.4.

In connection with their investigations on the proteolytic enzymes of flour, Sharp and Elmer (1924) found that the proteolytic enzymes of wheat flour will act on the flour protein if given sufficient time. The potassium-sulphate soluble protein increased steadily from the first to the fifth week. The amino nitrogen fraction increased from 4 to 5 times the first week and continued to show a small increase up to the fifth week. The gliadin fraction decreased notably the first week but

Fig. 4. Baking results with flour No. 121988 (two months after tests illustrated in Fig. 1 were made). It shows the effects on crumb structure produced by diastase of malt and also the influence of an aqueous extract of an equivalent quantity of this diastase when heated for 1 hour at 65° C., and not heated. The saccharogenic index of this sample of diastase was 645. It also possessed a high proteolytic activity.

showed only a slight decrease thereafter. The glutenin fraction remained essentially the same. The potassium-sulphate soluble fraction contained most of the protein split products.

Kawakami (1929) reported on proteolytic and amylolytic changes in Taka-diastase solution when the solution was kept at a moderately high temperature. At 55° C. proteolysis was most rapid, particularly during the first 1 to 2 hours. After 6 hours this activity had practically

ceased. At 45° C. proteolytic action was very slow and was still in progress after 80 to 90 hours. At 65° C. or above no appreciable increase in alkali number or formol number was observed, showing that the proteases did not act at 65° C. At 75° C. the amylolytic change was very rapid, but at this temperature the rate of reaction decreased rapidly. After 2 minutes it had fallen to ¼, after 6 minutes to 1/50, and had ceased after 60 minutes.

Fig. 5. Baking results with flour No. 121182, showing effects on crumb character produced by diastase of malt, and by yeast autolysate when added to the sponge mix as indicated on tag attached to loaf.

Tissue and Bailey (1931) published studies dealing with the proteolytic enzymes of malt preparations. They conducted their investigations in four directions, *viz.*, (1) removal of proteases from malt preparations; (2) comparison of the proteolytic activity of medium and high diastatic malts; (3) the diastatic potency of malt preparations following removal of the proteases; and (4) the comparative baking values of malt preparations in relation to their proteolytic activity. They re-

ported that diastatic malt preparations have a relatively high protease content and that the proteolytic activity of malt preparations may produce an inferior grade of bread if the product is incorporated in quantities sufficient to improve the diastatic activity of the dough. The proteases of diastatic malt were precipitated by safranine without appreciably reducing the diastatic activity of the malt, and an active proteolytic preparation was obtained from the precipitate.

Fig. 6. Baking results with flour No. 121944, showing the effects on crumb structure produced by additions of yeast autolysate (Y.A.) to the sponge. The saccharogenic capacity of the autolysate was practically negligible, but it possessed a marked proteolytic activity.

Experimental

Preliminary tests were made with varying amounts of the different enzyme preparations to determine the more desirable quantities to be added to the dough mixes. Different brands of bread flours which were notably "bucky" in their baking behavior were subjected to numerous baking tests with these enzyme preparations. The baked bread was

then examined and scored in the usual manner. In many instances photographs were taken of the cut loaf in order to have a more definite record of the crumb character.

In connection with the baking tests all straight doughs were made up in accordance with the following formula:

Flour	700 gms.
Water	sufficient
Yeast	12 gms.
Arkady	2 "
Salt	12 "
Sugar	28 "
Lard	14 "

These doughs were then carried through our standard laboratory procedure for the usual short and long fermentation periods, which differed about 30 minutes.

Responses of sponge doughs were the more outstanding. The action of the enzyme preparations was most marked when they were added to the sponge. The sponge time was made 3½ hours instead of the customary 4½ hours, after it was shown the additional hour produced no appreciable difference in the final results. The dough time was 20 minutes with an extra 25 minutes for the longer fermentation. The following formula was used:

Sponge		*Dough*
420 gms.	Flour	280 gms.
adequate	Water	sufficient
10 gms.	Yeast	——
3 "	Arkady	——
——	Salt	12.25 gms.
——	Sugar	28 "
——	Lard	14 "

As shown, the sponge mix was made with 60% of the flour, and received 60% of the total absorption plus 15 cc. In all cases the enzyme products were dissolved in water as far as possible prior to their addition. This practice was adopted to insure a uniform distribution of the enzyme throughout the sponge mix. The quality of the enzyme products used was as follows: diastase of malt (Merck—medicinal U.S.P.); pepsin (Merck—U.S.P.); papain (Merck); trypsin (Pfanstiehl—1:75).

The values given for saccharogenic activity were determined gravimetrically in accordance with the Blish *et al.* (1932) modification of the Rumsey procedure, using an acetate buffer solution. The tables which follow present an average of the results from three or more separate bakes. The last of the tables gives a brief characterization of the various enzyme preparations used. The photographic illustrations show more definitely the changes which were effected in crumb structure.

Discussion

The data presented in Tables I to IV inclusive, illustrate the effects produced on "bucky" doughs by certain proteolytic enzymes during the processes of fermentation and baking. The improvements noted in most instances are obviously to be attributed to the action of the proteases on the gluten. Baking tests with appropriate quantities of yeast autolysate added to the sponge further support this viewpoint. The proteolytic power of the autolysate was notably high while its saccharifying activity as determined by the Blish procedure was almost negligible.

TABLE I

BAKING TESTS WITH SPONGE DOUGHS.

(Scaling weight 500 gms. Enzyme preparations added to sponge)

Enzyme product	Amount added	Loaf volume	Texture	Grain	Ovenspring
		Cc.	*Score*	*Score*	
Flour No. 121944—Saccharogenic activity 215					
Control	None	1915	95	95	Poor
Diastase of malt	0.10 gms.	2057	98+	98	Poor
" " "	0.20 "	2233	100	99+	Fairly good
" " "	0.30 "	2419	100+	100	Good
Papain	0.028 "	2310	100	100	Fairly good
Barley malt flour II	0.35 "	1946	96+	96+	Poor
Yeast autolysate	4 cc.	2317	100	99+	Fairly good
" "	6 "	2322	100	100−	Fairly good
" "	8 "	2366	100	100	Good
Flour No. 121988—Saccharogenic activity 314					
Control	None	1910	95	95	Poor
Diastase of malt	0.30 gms.	2478	100	100	Good
" " "	0.35 "	2471	100	100	Good
Barley malt flour II	0.10 "	2030	97	96	Poor
" " " "	0.20 "	2025	97	96	Poor
" " " "	0.70 "	2030	97	96+	Poor
" " " "	1.40 "	2040	97	97	Poor
Yeast autolysate	6 cc.	2480	100	100	Good
" "	8 "	2494	100	100−	Good
" "	10 "	2510	100	100−	Good
Flour No. 121457					
Control	None	1862	94−	94	Poor
Diastase of malt	0.10 gms.	2163	99−	99	Fair
" " "	0.20 "	2282	100−	100	Fairly good
" " "	0.30 "	2492	100	100	Good
" " "	0.15 "				
Papain	0.028 "	2338	100−	100−	Good

Furthermore, the marked mellowing influence of the protease of commercial diastase of malt is particularly noteworthy. Also, similar benefits resulted from the use of papain, pepsin, and trypsin, but in

TABLE II

BAKING TESTS WITH SPONGE DOUGHS.

(Scaling weight 500 gms. Enzyme preparations added to sponge.)

Enzyme product	Amount added	Loaf volume	Texture	Grain	Ovenspring
		Cc.	*Score*	*Score*	
Flour No. 119988—Saccharogenic activity 255					
Control	None	1920	96	97	Poor
Diastase of malt	0.20 gms.	2366	100	99+	Good
" " "	0.30 "	2485	100	100+	Good
Papain	0.035 "	2330	100	100−	Good
Pepsin	0.070 "	2373	100	100−	Good
Diastase of malt	0.20 "				
Papain	0.014 "	2331	100	100	Good
Diastase of malt	0.20 "				
Pepsin	0.028 "	2415	100	100	Good
Diastase of malt	0.20 "				
Pepsin	0.042 "	2408	100	100	Good
Papain	0.021 "				
Pepsin	0.035 "	2340	100	100−	Good
Papain	0.021 "				
Pepsin	0.035 "	2380	100	100−	Good
Diastase of malt	0.20 "				
Barley malt flour I	0.350 "	2058	97	96	Poor
Barley malt flour II	0.350 "	2100	97	96	Poor
Wheat malt flour E	0.350 "	2090	97	96	Poor
Barley malt flour II	1.40 "	2140	98	97+	Fair
Wheat malt flour E	1.40 "	2002	98	97−	Poor
Flour No. 121182—Saccharogenic activity 181					
Control	None	1895	95	96	Poor
Diastase of malt	0.30 gms.	2485	100	100	Good
" " "	0.35 "	2450	100	100+	Good
Powdered extract of malt	2.10 "	2128	97	97−	Fair
" " " "	3.50 "	2156	97	97	Fair
Malt syrup—123114	7.00 "	1869	95	96	Poor
" " —123114	26.50 "	2083	97	96+	Fair
" " —123115	7.00 "	1948	96	96	Poor
" " —123115	10.50 "	1988	95+	95+	Poor
" " —123116	7.00 "	2020	96+	96+	Fair
Yeast autolysate	5 cc.	2429	100	100−	Good

decreasing degree. The improvements noted in the "feel" of the treated doughs likewise varied in extent. The diastase treated sponge mixes produced the finer feeling and more lively doughs. Those treated with papain showed the next best improvement. The animal proteases,

pepsin and trypsin, were less effective, but even these preparations exerted marked benefit on the dough when used in suitable dosages.

On the contrary, in the case of sponge doughs, like improvements could not be obtained by the use of malt flours from wheat or from barley. The malt flours were high in diastatic activity as shown in Table V, but were notably low in protease content (action on gelatin) in comparison with such preparations as papain and commercial diastase. If the starch liquefying power of these malt flours parallels their sac-

TABLE III

BAKING TESTS WITH SPONGE DOUGHS.

(Scaling weight 500 gms. Enzyme preparations added to sponge. One cc. of extract equivalent to 100 mgs. of original material.)

Enzyme product	Amount added	Loaf volume	Texture	Grain	Ovenspring
		Cc.	*Score*	*Score*	
Flour No. 121988—Saccharogenic activity 314					
Control	None	1827	95	94	Poor
Diastase of malt	0.32 gm.	2422	100+	100	Good
Water extract of diastase, not heated	3.5 cc.	2366	100+	100	Good
Water extract of diastase, heated 1 hour at 65° C.	3.5 "	2107	99−	97	Fair
Water extract of diastase, heated 1 hour at 65° C.	10.5 "	2046	97	96−	Fair
1% lactic acid extract of diastase, not heated	3.5 "	2086	97+	96−	Fair
1% lactic acid extract of diastase, not heated	10.5 "	2205	99	98	Fairly good
1% lactic acid extract of diastase heated 1 hr. at 65° C.	3.5 "	2110	97	97	Fair
1% lactic acid extract of diastase heated 1 hr. at 65° C.	7.0 "	2110	97	97	Fair
1% lactic acid extract of diastase heated 1 hr. at 65° C.	10.5 "	2070	97	96	Fair

charifying capacity, the failure of these malt flours to materially improve the quality of bread when added either to the sponge or to the straight dough is possibly to be attributed to two factors—(1) the production of large quantities of the more or less soluble dextrins resulting from the liquefying component of the diastase (particularly during the initial stages of baking), and (2) to the absence of sufficient proteolytic activity to cause any appreciable mellowing of the gluten complex, although the malt flours were obviously normal in their content of protease.

TABLE IV

BAKING TESTS WITH STRAIGHT DOUGHS.

(Scaling weight 475 gms. Bread score figures represent an average of the long and short fermentations.)

Enzyme product	Amount added	Loaf volume	Texture	Grain	Ovenspring
	Gms.	*Cc.*	*Score*	*Score*	
Flour No. 117000					
Control	None	2331	100	98+	Good
Diastase of malt	0.070	2370	100	100	Good
Papain	0.035	2290	100	99	Fairly good
Pepsin	0.035	2352	100	99	Good
Trypsin	0.035	2352	100	99	Good
Papain	0.028				
Diastase of malt	0.070	2320	100	100+	Good
Papain	0.035				
Diastase of malt	0.070	2226	100	100	Fairly good
Pepsin	0.035				
Diastase of malt	0.070	2335	100	100	Good
Pepsin	0.056				
Diastase of malt	0.070	2310	100	100	Good
Trypsin	0.056				
Diastase of malt	0.070	2331	100	100−	Good
Wheat malt flour B	1.40	2359	100	99+	Good
Wheat malt flour B	2.80	2400	100	99+	Good
Wheat malt flour E	1.40	2380	100	100	Good
Flour No. 117001					
Control	None	2380	100−	98+	Good
Papain	0.028	2300	100+	100	Fairly good
Papain	0.028				
Diastase of malt	0.035	2408	100	100	Good
Papain	0.028				
Diastase of malt	0.070	2410	100+	100+	Good
Papain	0.035				
Diastase of malt	0.070	2513	100+	100	Good
Trypsin	0.035				
Diastase of malt	0.070	2440	100+	100−	Good
Diastase of malt	0.035	2331	100+	100−	Good
Diastase of malt	0.070	2380	100+	100−	Good
Flour No. 119304—Saccharogenic activity 325					
Control	None	2338	100	98−	Good
Papain	0.028	2290	100	100	Fairly good
"	0.035	2170	100	100−	Fair
Papain	0.028				
Diastase of malt	0.070	2215	100	100−	Fair
Papain	0.035				
Diastase of malt	0.070	2205	100	100−	Fair
Pepsin	0.070	2352	100	100	Good

TABLE IV—*Continued*

Enzyme product	Amount added	Loaf volume	Texture	Grain	Ovenspring
	Gms.	*Cc.*	*Score*	*Score*	
Flour No. 119304—Saccharogenic activity 325					
Pepsin + Diastase of malt	0.070 + 0.070	2408	100+	100	Good
Trypsin	0.070	2254	100−	100−	Fairly good
Trypsin + Diastase of malt	0.070 + 0.070	2285	100	100−	Fairly good
Diastase of malt	0.070	2422	100	100−	Good
Flour No. 119305—Saccharogenic activity 322					
Control	None	2065	98	96	Poor
Papain	0.028	2184	100	100−	Fair
Papain	0.035	2200	100	100−	Fair
Papain	0.042	2178	100	100−	Fair
Pepsin	0.070	2300	100+	100−	Fairly good
Trypsin	0.070	2235	100	98+	Fair
Papain + Diastase of malt	0.028 + 0.070	2219	100	100−	Fair
Papain + Diastase of malt	0.035 + 0.070	2190	100	100	Fair
Pepsin + Diastase of malt	0.070 + 0.070	2170	100	100	Fair
Trypsin + Diastase of malt	0.070 + 0.070	2165	100	100−	Fair
Diastase of malt	0.070	2100	99+	99−	Poor
Barley malt flour I	1.40	2185	100	99	Fair
Barley malt flour II	1.40	2212	100	99	Fair

The baking results were essentially the same with these flours whether used in small or relatively large quantities, with the exception that large dosages produced excessively sticky doughs. On the basis of data on hand, it appears that the trouble which arises from an overdosage of a normal malt flour should be assigned to its starch liquefying capacity rather than to its saccharifying power. More technical studies on these particular phases of the problem are now being pursued in this laboratory.

The beneficial factors in commercial diastase are soluble in water, at least the major portion. When an aqueous extract was used in quantities equivalent to the amounts added in the dry state, the same favorable results were obtained in the baking tests. The aqueous extract possessed the same relative proteolytic activity as measured by its liquefying action on gelatin. Heating the extract for one hour at 65° C. caused the destruction of most of its proteolytic and saccharifying

power. A corresponding extract of the diastase with a 1% lactic acid solution was much less potent in proteolytic and saccharifying power as indicated by the results of baking tests with these extracts in Table IV.

Animal proteases such as pepsin and trypsin do not have a favorable pH for their action in a dough mix. In the quantities used pepsin exerted a more favorable action on the dough than did trypsin. The effect on the dough characteristics was in the same favorable direction, however, as that of papain or diastase.

Other diastatic products such as powdered malt extract and malt syrups of varying degrees of saccharifying power were also tested. Their action in "bucky" sponge doughs was no more beneficial than

TABLE V

DIASTATIC ACTIVITY OF CERTAIN PRODUCTS USED IN TESTS

Product	Diastatic activity of product[1]	Saccharogenic index[2]	Flour used in determining saccharogenic index
			No.
Barley malt flour I	1387	317	119304
Barley malt flour II	1655	382	119304
Barley malt flour II	—	350	119988
Wheat malt flour B	1365	448	115576
Wheat malt flour E	1762	472	116931
Merck's diastase of malt	—	645	119988
Yeast autolysate	—	22	121944
Malt syrup—123114—20° L.	—	57	121182
" " —123115—60° L.	—	102	121182
" " —123116—120° L.	—	164	121182

[1] According to Rumsey-Blish.

[2] By the term "saccharogenic index" is meant the number of milligrams of anhydrous maltose yielded by 10 gms. of flour when allowed to digest with 1% of the active agent for one hour at 30° C., *e.g.*, 100 mgs. (1%) of barley malt flour I produced 317 mgs. of anhydrous maltose from 10 gms. of flour No. 119304 in one hour at 30° C. The index of a given product usually shows some variation with different flours.

that of the malt flours. Their proteolytic activity on gelatin was practically nil. In bakes from straight doughs, however, the influence of the more potent syrups on a tough gluten was somewhat more noticeable, but was not comparable to the effects produced by diastase of malt, papain, or pepsin.

In preparing the photographic illustrations which follow, the chief aim was to show comparative differences in crumb structure, rather than comparative differences in volume and oven-spring. Therefore, such minor adjustments were made in focussing the camera as were necessary to best portray the internal character of the loaf. The volume is shown in cubic centimeters. The photographs represent cross-section through center of the loaf.

Summary

Experimental data are presented which illustrate the beneficial effect of the proteolytic action of certain enzyme preparations on the baking behavior of flour giving rise to "bucky" doughs. The gluten character of such flours is the factor chiefly responsible for the inferior volume, coarse grain, and frequent occurrence of large holes which usually characterize the bread produced from "bucky" doughs.

The most interesting observation was the marked mellowing action exerted on the gluten by small amounts of several of the proteolytic products used. This was particularly noticeable in the case of sponge mixes, and resulted in the production of a drier, more lively, and better working dough, which gave loaves of high quality.

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METHODS FOR DETERMINING THE VISCOSITY OF FLOUR-IN-WATER SUSPENSIONS

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Introduction

At the present time many cereal chemistry laboratories are using the viscosity test to aid in determining flour characteristics. However, no standard procedure has been developed which is accepted and used by all laboratories. As a result of this condition, the value of the viscosity test to the cereal chemist is not fully appreciated.

This investigation was undertaken to develop a reliable laboratory method for the measurement of the viscosity of flour-in-water suspensions. The method selected should be rapid, relatively simple, and capable of producing accurate results which can be translated into terms of flour quality. The problem lies in the proper preparation of the flour sample and the technique to be used in determining the viscosity.

The methods in general use consist of preparing the samples either by grinding with water in a mortar and then measuring the increase in viscosity caused by successive additions of normal lactic acid, or shaking the sample with the proper quantity of water in an Erlenmeyer flask, allowing it to stand for a time and then measuring the viscosity after one addition of normal lactic acid.

When used continuously by a laboratory either of these methods will give the desired information. However, it is difficult for a laboratory using one method to properly translate the results of a laboratory using another method. Laboratories using the same method have encountered trouble in duplicating each other's results on the same samples of flour. A method of determining the viscosity of flour-in-water suspensions which would eliminate the difficulties mentioned above would be very desirable.

Historical

There are two outstanding investigations on flour viscosity, that of Lüers and Ostwald (1919), and Sharp and Gortner (1923). Lüers and Ostwald performed their first viscosity work in Ostwald viscosi-

meters. The running through time of specially prepared gelatinized flours as compared with the running through time of water was taken as a measure of the viscosity. They studied the effect of concentration, acidity and type of water on the viscosity of dilute dough solutions. Ostwald and Lüers showed that a small increase in concentration effected a large increase in viscosity, that with a wheat dough of 60% extraction, the presence of 0.5 normal lactic acid causes an increase in viscosity of about 450%, that $CaSO_4$ water (20° German hardness CaO) decreased the viscosity, and Ca $(HCO_3)_2$ and Mg $(HCO_3)_2$ (both 20° German hardness CaO) increased the viscosity.

Sharp and Gortner, using flour-in-water suspensions, criticised the use of the Ostwald viscosimeter and used the MacMichael instrument instead. They studied the viscosities of flours at various hydrogen-ion concentrations and concluded that maximum viscosity occurs at approximately the same pH regardless of the acid used and that maximum peaks of viscosity occur at pH3 and pH11. They decided that lactic acid is the best because it effects the least change in viscosity per unit of actual acid concentration. Although their work extended over a period of several months, Sharp and Gortner concluded that as long as the flour was stored at a low temperature (3 to 5° C.), age made no noticeable effect on the results.

Smith (1925) using a Sheely pipette viscosimeter and working with ten flours of different types and grades found that all the flours having a high viscosity were of excellent baking quality. The flours of low viscosity were found to range from excellent to poor in baking quality. From a survey of 110 flours of the 1922 Nebraska wheat crop, Blish and Sandstedt (1925) found that perhaps the most valid criticism which can be applied to viscosity measurements on acidified flour-in-water suspensions is that such suspensions are generally subject to the laws of plastic rather than viscous flow. Bingham (1925) said, "One must not expect useful information from determinations of apparent viscosity if the material dealt with is really plastic in character."

After running several thousands of tests on many different brands and grades of flour with the MacMichael viscosimeter, Sasse and Pearson (1930) conclude that the viscosity test adds nothing to the information obtained from the protein and ash determinations and can never be made to replace the baking test. Bayfield (1934) working with 100 experimentally milled Ohio soft winter wheat flours finds that loaf volume is positively correlated with both protein content and viscosity, and since loaf volume is an acceptable measure of strength the viscosity test may offer some possibilities as a substitute for the baking test.

Material and Methods

Materials

Flour milled from four distinct types of wheat into four different grades were studied in this investigation. The types and grades of flours used are listed in Table I along with their protein and ash con-

TABLE I

DESCRIPTION OF FLOURS USED IN THIS INVESTIGATION

Flour number	Type of wheat	Grade	Ash[1]	Protein[1]	Volume of test loaf
			P.ct.	*P.ct.*	*Cc.*
1	Indiana red (*a*)	5% low grade	1.031	11.49	270
2	Indiana red (*b*)	35% clear	.470	9.33	380
3	Indiana red (*c*)	60% patent	.28	7.67	355
4	Indiana red (*d*)	100% straight	.458	8.72	380
5	Michigan soft red and white (*a*)	36% clear	.462	8.57	375
6	Michigan soft red and white (*b*)	100% straight	.418	8.22	370
7	Michigan soft red and white (*c*)	5% low grade	.618	9.57	410
8	Michigan soft red and white (*d*)	Short patent	.334	8.16	370
9	Idaho red (*a*)	100% straight	.435	12.47	415
10	Idaho red (*b*)	60% patent	.328	11.56	420
11	Idaho red (*c*)	35% clear	.596	14.44	415
12	Idaho red (*d*)	5% low grade	1.283	16.01	285
13	Pacific Coast Bluestem (*a*)	100% straight	.433	11.59	420
14	Pacific Coast Bluestem (*b*)	60% patent	.366	10.67	420
15	Pacific Coast Bluestem (*c*)	35% clear	.529	13.26	375
16	Pacific Coast Bluestem (*d*)	5% low grade	.939	15.68	310

[1] 15% H_2O basis.

tents, and volume of loaf as determined by the basic A. A. C. C. baking test.

FLOUR TYPE 1. These flours were milled from Indiana soft red winter wheat. They were unbleached.

Flour (*a*) was a 5% low grade, of inferior baking quality, and extremely dark in color.

Flour (*b*) was a 35% clear. This flour while showing satisfactory characteristics for a soft red winter wheat was not of good quality.

Flour (*c*) was a 60% patent. This flour was considerably better in color as well as quality when compared with the other flours of this group.

Flour (*d*) was a 100% straight. This flour was quite similar in characteristics to the 35% clear. However, it was slightly better in quality than the clear.

FLOUR TYPE 2. These flours were milled from mixed Michigan red and white wheats. The flours were bleached.

Flour (*a*) was a 36% clear, quite soft in texture, but not of very good quality.

Flour (*b*) was a 100% straight, somewhat better in quality than the 36% celar, but of the same general characteristics.

Flour (*c*) was a 5% low grade. This was the strongest low grade used in these studies.

Flour (*d*) was a short patent (percentage extraction unknown). The superior quality of this flour over all other flours of this group was apparent.

FLOUR TYPE 3. These flours were milled from Idaho hard red winter wheat.

Flour (*a*) was a 100% straight grade; while it was the strongest flour of group, it was mediocre in quality. The test loaf had a rather deep crust color, but did not exhibit much oven spring.

Flour (*b*) was a 60% patent. This flour was considerably superior in quality and color to the other flours in this series.

Flour (*c*) was a 35% clear. This flour was similar in characteristics to the straight grade flour but of inferior quality, the bread made therefrom being characterized by a dull color and coarse grain and texture.

Flour (*d*) was a 5% low grade, typical of this class of flours. Test loaves from this flour were low in volume and the crumb was very dark in color.

In this group of flours the differences between grades was more pronounced than in the flours milled from wheats mentioned as types 1 and 2.

FLOUR TYPE 4. These flours were milled from Pacific Bluestem wheat, a hard white wheat grown in Oregon.

Flour (*a*) was a 100% straight grade, medium strong and of fairly good diastatic strength.

Flour (*b*) was a 60% patent. Although similar in characteristics to flour (*a*) it was better in color and quality.

Flour (*c*) was a 35% clear, of inferior quality.

Flour (*d*) was a 5% low grade.

Methods

Three different methods for measuring the viscosity of the flour-in-water suspensions were investigated. The MacMichael viscosimeter

operated with a cup speed of 12 r.p.m. and a No. 30 wire (B. & S. gauge) was used in all the tests. All the readings were taken in degrees MacMichael and are therefore comparable only among themselves.

Method A. The moisture content of the flour was determined and an equivalent weight of 20 gms. of the sample corrected to a 15% moisture basis was used for the viscosity test. The amounts of flour used for methods *A*, *B*, and *C* are given in Table II. The sample was pre-

TABLE II

MOISTURE CONTENT OF FLOUR AND WEIGHT USED FOR VISCOSITY TESTS

Sample number	Moisture	Sample weight[1]		Sample number	Moisture	Sample weight[1]	
		Method *A*	Methods *B* & *C*			Method *A*	Methods *B* & *C*
	P.ct.	*Gms.*	*Gms.*		*P.ct.*	*Gms.*	*Gms.*
1	11.42	19.20	16.70	9	12.10	19.30	15.51
2	12.20	19.40	20.74	10	11.97	19.30	16.70
3	12.15	19.35	25.25	11	12.28	19.40	13.42
4	11.88	19.30	22.12	12	10.57	19.10	11.91
5	11.58	19.20	22.45	13	11.59	19.00	16.41
6	12.46	19.40	23.63	14	11.81	19.30	18.07
7	11.97	19.30	20.18	15	11.62	19.20	14.50
8	12.13	19.30	23.70	16	10.94	19.10	12.17

[1] 15% H_2O basis.

pared in the manner described in procedures 1 or 2 described below, and poured into the viscosimeter cup. The suspension was stirred for 15 seconds with the bob, while the cup was rotating. The bob was then hung in position and a reading was taken. 1 cc. of normal lactic acid was added with a suitable pipette. The material was stirred for 10 seconds and a second reading was taken. Three subsequent readings were taken in the same manner as described, except that 2 cc. of acid was added instead of 1. The total amount of acid used was 7 cc. The difference between successive viscosity readings was plotted against the number of the reading.

Method B. This method is the same as "*A*" except that a weight of sample equivalent to 2 gms. of protein was used.

Method C. This method differs from the other two in that only one viscosity reading was taken. A weight of sample equivalent to 2 gms. of protein was prepared according to procedure 3 described below. This suspension was allowed to stand for 45 minutes after which 5 cc. of lactic acid was added and stirred into the mixture. After 5 minutes the material was poured into the viscosimeter cup, stirred with the bob for 15 seconds, and a single reading taken.

Procedure for preparing the flour-in-water suspensions

1. The proper amount of sample was placed in a mortar. 70 cc. of distilled water was added and the flour thoroughly wetted by stirring with a small spatula. The mixture was then worked into a smooth suspension with a pestle. 20 cc. more of water was added and stirred into the suspension. The material was poured into the viscosimeter cup and the mortar rinsed with the remaining water which was then added to the suspension in the cup. The total amount of water used was 100 cc.

2. This method makes use of a mechanical stirrer. 35 cc. of distilled water was placed in a porcelain cup with the proper amount of flour. The stirrer speed was adjusted to about 200 r.p.m. by a resistance in series with the motor, and the flour and water stirred for one minute. The stirrer was then removed and cleaned of any flour that might adhere to it. 50 cc. of water was added and stirred into the suspension. The material was poured into the viscosimeter cup and the remaining water was used to rinse the mixing cup, after which it was added to the material for the viscosity test. A total of 100 cc. of distilled water was used.

3. The sample of flour to be tested was placed in a 300 cc. Erlenmeyer flask with 90 cc. of distilled water. The flask was shaken until a smooth suspension resulted. The suspension was poured into the viscosimeter cup and the remaining 10 cc. of water used to rinse the flask.

Experimental Results

The results of the viscosity tests by methods *A* and *B* are shown graphically in Figures 1 to 8 inclusive. The results by method *C* are reported in Table III with the end point readings from methods *A* and *B*.

It was found during the investigation that if duplicate tests were made within a short time of one another satisfactory checks could be obtained. However, if the readings were taken within several days of one another the results could not be duplicated. A careful check was made of all the mechanical features of the test, but none of these were found to be at fault. An investigation was then undertaken to determine whether the lactic acid might be causing the discrepancies in the results.

A fresh supply of acid was made up in the usual manner, and adjusted to exactly normal. Duplicate viscosity tests were made on the 60% patent Indiana red wheat flour. The solution was divided into two parts, one of which was kept in the laboratory at 26° C. and the

TABLE III

VISCOSITY READINGS BY METHOD *C* AND END POINT READING FROM METHODS *A* AND *B*

Sample number	Viscosity reading	End point		Sample number	Viscosity reading	End point	
	Method *C*	Method *B*	Method *A*		Method *C*	Method *B*	Method *A*
	°*MacM.*	°*MacM.*	°*MacM.*		°*MacM.*	°*MacM.*	°*MacM.*
1	15	12	20	9	62	100	177
2	107	86	70	10	120	138	207
3	115	147	72	11	71	48	115
4	100	88	60	12	9	5	25
5	66	54	38	13	109	78	114
6	50	56	33	14	118	110	132
7	48	41	45	15	84	62	106
8	74	73	42	16	22	14	36

other in the refrigerator at 4° C. The change in normality of the acid was observed at intervals for a period of a month. At the same time the strength of the acid was determined, viscosity tests by method *A* were made on the 60% Indiana red wheat flour with each batch of acid.

It was found that the acid which was kept in the room increased in normality from 1.000 to 1.185, and was continuing to increase at the end of the month. The acid which was kept in the refrigerator increased in normality, but not to as great a degree as that kept in the room. The range in normality of the refrigerated acid was from 1.000 to 1.057. These results are shown graphically in Figure 9.

The viscosity readings made on the 60% Indiana red wheat flour after the acid was three days old were lower than original values, but subsequent tests showed a gradual increase. Figure 10 shows the increase over a period of a month in the difference between the viscosity of the flour-water suspension and after the addition of 1 cc. of the lactic acid.

In order to overcome the change in normality a different method of preparing the normal lactic acid was developed. Enough concentrated lactic acid was used to prepare a solution which was approximately 0.8500 N when standardized with N/10 NaOH. This solution was transferred to an Erlenmeyer flask, fitted with an air condenser to prevent undue evaporation of water, and heated at a temperature of 80° C. for 24 hours. At the end of this time it was found that the solution had increased in strength to 1.183 N. Enough distilled water was added to bring the solution to exactly normal.

The normality of this solution was determined at three-day intervals and viscosity tests were made on the 60% Indiana red wheat flour using

this acid. The results show that the normality of the acid did not increase, and satisfactory checks were obtained from the viscosity test.

Procedure 1 was considered to be the best way to prepare the flour in water suspension. Method B was chosen the most desirable for measuring the viscosity of the flour-in-water suspension.

Discussion of Results

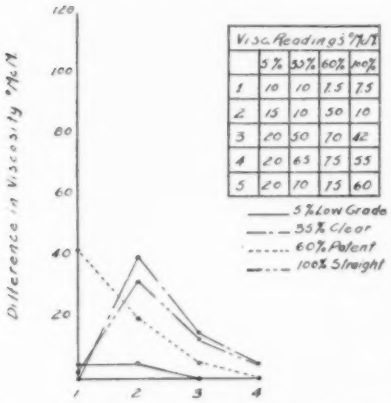
The Viscosity Curves

A study of Figures 1 to 8 shows that the viscosity curve of the same grade of flour from any of the four types has the same general shape. The 5% low grade flours show only a slight increase in viscosity on the addition of lactic acid. This is due principally to the buffer action of mineral matter and the poor quality of the protein in this grade of flour. The viscosity curves of all the 35% clear flours have the shape of an inverted V. The increase in viscosity on the addition of 1 cc. of lactid acid is either zero or very small. The difference between the second and third readings is considerable, showing that the buffer action of the mineral matter had been overcome and activation of the proteins begun. The third addition of acid caused a further increase in viscosity, but not as much as the second. This is shown by the negative slope of the curve between points 2 and 3. The fourth addition of acid caused a slight increase in viscosity in some cases, no increase in others, and some flours showed a decrease in viscosity at this point. The decrease in viscosity is probably due to peptization of the proteins.

The curves from the 100% flours closely parallel those from the 35% clears. However, in every case the first difference in viscosity is greater than that for the 35% flours. This is an indication that the mineral matter in the 100% flour is less than that in the 35%. The analysis of the samples shows this to be true. The difference in viscosity between the third and fourth additions of acid is in general less than the corresponding difference for the 35% grades. Because of the lower mineral content, the maximum viscosity of the 100% flour is reached before that of the 35% grade.

The viscosity curves of the 60% patent flours are all more or less L shaped. This indicates that the greatest increase in viscosity occurs on the first addition of lactic acid. The second and third additions of lactic acid produce progressively smaller increases in viscosity. On all of the 60% samples except the Idaho red wheat, the fourth addition of acid caused either no increase or a slight decrease in viscosity.

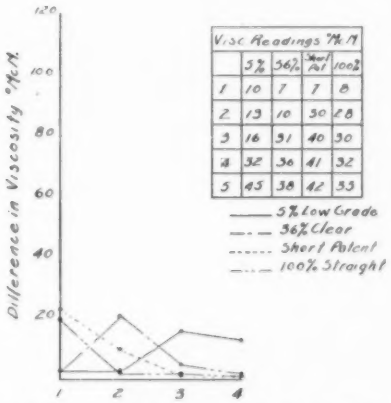
The results obtained by method C, although slightly higher, correspond to the final viscosity readings of method *B*. The greater reading



Visc. Readings °/₀₀ N.

	5%	35%	60%	100%
1	10	10	15	15
2	15	10	30	10
3	20	30	70	42
4	20	65	75	55
5	20	10	75	60

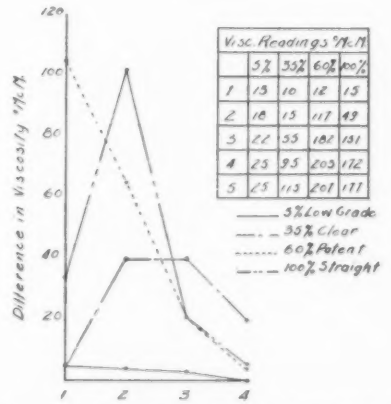
Fig. 1. Viscosity curves, Indiana red wheat, Method A.



Visc. Readings °/₀₀ N.

	5%	36%	Short Pat	100%
1	10	7	7	8
2	13	10	30	28
3	16	31	40	30
4	32	36	41	32
5	45	38	42	33

Fig. 2. Viscosity curves, Michigan red and white wheat, Method A.



Visc. Readings °/₀₀ N.

	5%	35%	60%	100%
1	13	10	12	15
2	18	15	117	49
3	22	55	182	131
4	25	95	203	172
5	25	113	201	171

Fig. 3. Viscosity curves, Idaho red wheat, Method A.

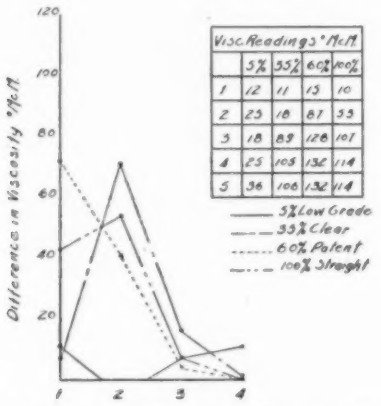


Fig. 4. Viscosity curves, Pacific Coast blue stem, Method A.

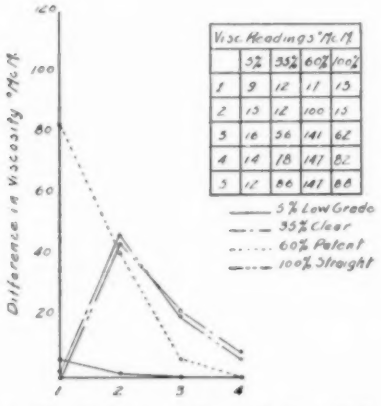


Fig. 5. Viscosity curves, Indiana red wheat, Method B.

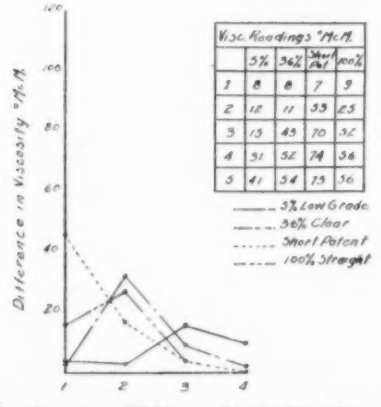


Fig. 6. Viscosity curves, Michigan red and white wheat, Method B.

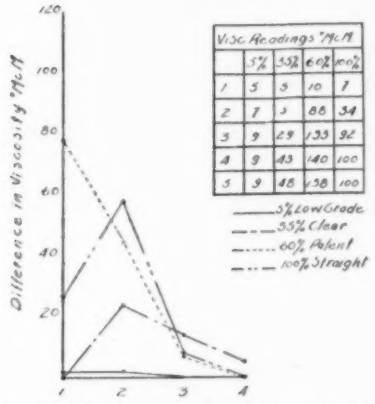


Fig. 7. Viscosity curves, Idaho red wheat, Method B.

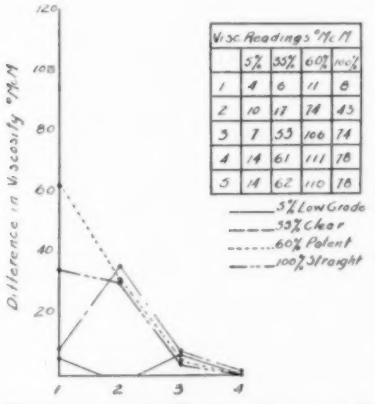


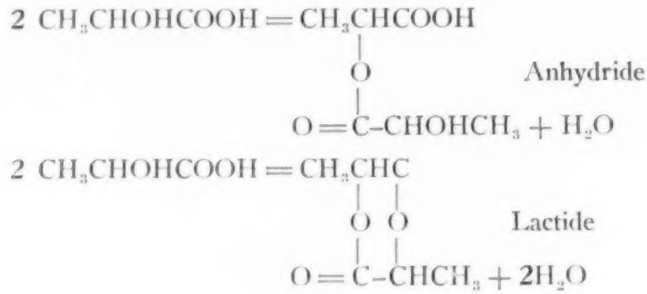
Fig. 8. Viscosity curves, Pacific Coast blue stem, Method B.

is probably due to the increased time of contact between the flour and the acid.

A comparison of the analytical and baking test data with the viscosity curves shows that the viscosity determination can be used to indicate both the type and grade of a given flour. The general shape of the curve, with particular emphasis on the first difference in viscosity, is an indication of the grade of the flour. The end point reading determines the type of the flour. An examination of the data shows that the end point readings of the flours milled from Idaho red wheat are higher than those of the other flours. The baking test showed the Idaho red wheat flour to be the strongest of the four types of flour used in this investigation. Next in strength, according to the baking test, are the flours milled from Pacific Coast Bluestem, followed by flours milled from the Indiana and Michigan wheats in the order named. The viscosity data also place the flours in this order according to their strength.

Increase in Strength of Lactic Acid

When in the concentrated form, two molecules of lactic acid react to form the lactide and water.



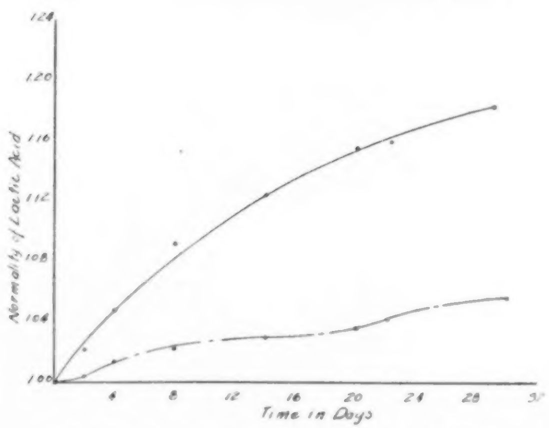


Fig. 9. Increase in normality of lactic acid with time.

On dilution with water both the anhydride and the lactide hydrolyze to form lactic acid—(Thurmond and Edgar, 1924). This explains the increase in strength of the lactic acid solution with age.

Because of the relatively low temperatures at which the acid was kept the rate of hydrolysis was retarded. The application of heat increased the rate of hydrolysis to such a degree that it was completed within 24 hours, and equilibrium established between the lactic acid and water. Once fixed, further dilution with water does not disturb the equilibrium.

Recommendations

The work of Sharp and Gortner indicated that a torsion type of viscosimeter was best for flour work. For this reason, and the fact that it has proven very satisfactory in this investigation, we suggest the use of the MacMichael viscosimeter for measuring the viscosity of flour-in-

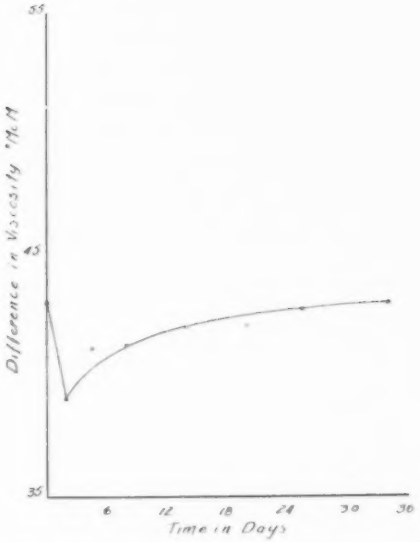


Fig. 10. Increase in viscosity with strength of lactic acid.

water suspensions. When the viscosimeter is operated with a cup speed of 12 r.p.m. and a No. 30 wire is used to support the bob, readings of convenient magnitude are obtained.

Procedure 1 for suspending the flour in water is suggested because of its simplicity and ability to produce smoother suspensions than either of the other two methods.

As far as their ability to produce results from which the general characteristics of a flour can be evaluated there is little to choose between either method *A* or *B* for measuring viscosity. Both methods produce the same type of viscosity curve. Method *C* gives an indication of the strength of gluten but gives no picture of the quality of the flour. Since the viscosity of flour-in-water suspensions is mostly affected by the condition of the proteins in the flour it seems most logical to eliminate protein quantity as a factor in the final result. For this reason we suggest the use of method *B* for the measurement of the viscosity of flour in water suspensions.

Summary

This investigation was undertaken to develop a reliable method for the measurement of the viscosity of flour in water suspensions. Three methods of preparing the suspension, and three methods for measuring the viscosity were used.

The selected method uses a weight of sample equivalent to two grams of protein. This quantity of flour is suspended in 100 cc. of water by the use of a mortar and pestle. A MacMichael viscosimeter using a No. 30 wire, and a cup speed of 12 r.p.m. is suggested. A viscosity curve is obtained by measuring the viscosity of the flour-in-water suspension and then the viscosity after acidulation first with 1 cc. of N/1 lactic acid, followed by three 2 cc. portions. The difference in viscosity between successive readings is plotted against a number equal to one less than the number of the reading.

The results of the investigation show that viscosity of flour-in-water suspensions, acidulated with lactic acid, can be used as a reliable means for determining the types and grades of wheat flours.

With the proper precautions, particularly with respect to the lactic acid, the results of the viscosity test can be readily duplicated.

The inability to check results after a lapse of several days can be traced directly to the condition of the lactic acid used, and not to the mechanical manipulations, provided they are performed with proper care.

Acknowledgments

The writer wishes to express his appreciation for technical assistance to George Garnatz and Mrs. B. Chandler of the Kroger Food Foundation, and Dr. E. F. Farnau of the University of Cincinnati. Thanks are also given to H. H. Wurtz of the Kroger Grocery and Baking Company, for obtaining the flour samples used in this work.

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USE OF THE GLASS ELECTRODE FOR DIRECT MEASUREMENT OF H-ION CONCENTRATION IN FERMENTING DOUGHS

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(Read at the Convention, June, 1933)

While satisfactory methods have been developed for the determination of H-ion concentration in cereal extracts, and to a certain extent in flour suspensions (Bailey (1930), Halton and Fisher (1928), Whittier and Grewe (1929), Holm and Grewe (1930), and Sorg (1930)), the determination of the pH value of doughs has offered some difficulty. The usual procedure has been to disintegrate the dough with distilled water and determine the pH in the resulting suspension or filtrate (Blish and Hughes, 1932). Halton and Fisher (1932) have adapted the ball quinhydrone method to this problem with but slightly irregular results. The use of an electrode which could be applied directly to the dough without the addition of any foreign ingredient would be of obvious convenience.

The Glass Electrode

The fact that certain glass membranes function reversibly as hydrogen electrodes has long been known, but satisfactory technique for utilizing this property awaited development by MacInnis and Dole (1930) of a suitable glass (Corning 015). These investigators developed a convenient electrode of small size with low asymmetry potential and sufficiently low resistance that small membrane areas could be used. A certain inconvenience, however, attended their use; they were fragile and easily polarized, and necessitated the use of a sensitive electrometer with rather elaborate shielding. In the attempt to eliminate the inconvenience of the use of the electrometer at least twenty vacuum tube circuits have been described. Most of these have the grid of the vacuum tube in the circuit of the cell, and thus a small continuous current is drawn from it. Even with special low grid current tubes in which the current drawn from the cell may be made as small as 10^{-14} amperes, polarization is likely to occur unless the membrane is very thin or large in area. In addition the galvanometer deflections obtained from this

type of circuit are subject to annoying fluctuations due to filament current changes and drifts in grid potential.

A sensitive and practical vacuum tube circuit for measurement of electromotive force through large resistances or systems which are easily polarized, has been described by Ellis and Kiehl (1933).[1] The device is simple, inexpensive, constructed of standard parts which are readily available, and in actual use has been found convenient, dependable, and rugged. A small capacity radio type air condenser (.001 microfarad) with amber insulation, together with the controlling switches, is enclosed in a dessicated (calcium chloride) chamber. This condenser is placed in series with the electrode and the grid of the first vacuum tube (4 type 233 tubes are used) and hence the current flowing through the cell between readings is limited only to the leakage current through the exceptionally high insulation resistance of the condenser (Figure 1).

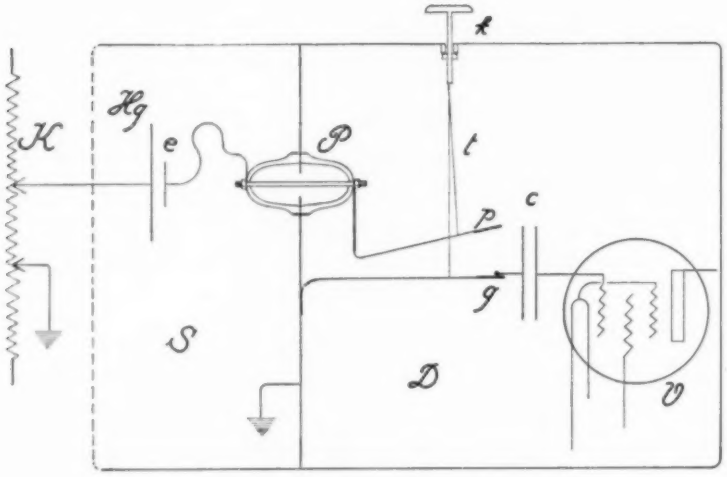

Fig. 1. The essentials of the Ellis and Kiehl Circuit.

K—Leeds and Northrup type K potentiometer
Hg—Calomel electrode
e—Glass electrode
S—Metal shield (Elaborate shielding has been found to be unnecessary)
p, g—High insulation switch
k—Tap key
t—Silk threads
c—Air condenser, original insulation replaced by amber
D—Dessicated chamber
V—Type 233 vacuum tube
P—Pyrex insulator

The smallest unbalanced potential giving a visible deflection through a resistance of 1000 megohms is 0.06 millivolts, while through even 100,000 megohms an unbalanced potential of 1.2 millivolts may be detected.

[1] Compare also Hemmingway and Arnow (1933).

In addition, since near the balance point the amount of electricity drawn from the cell is in the neighborhood of 10^{-12} coulomb, polarization effects are practically zero. This permits the use of relatively thick, rugged glass membranes suitable for introduction into the dough.

Preliminary experiments with the MacInnis and Dole (1930) type glass electrode, which seems most suitable for use in the dough, gave promising results. It was found, however, that the membrane was more suitably protected if placed as a window on the side of the tube. As a matter of convenience, the type of cell shown in Figure 2 was finally developed. In essence, this represents a combination of the side window

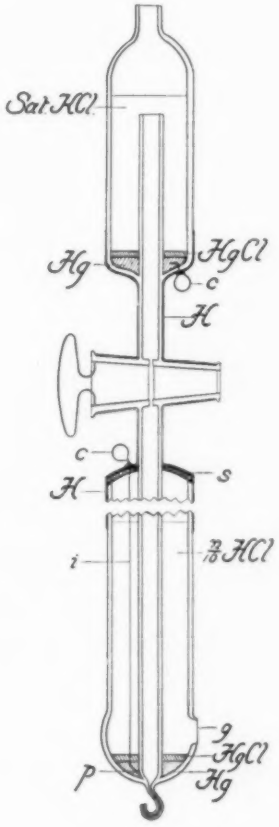

Fig. 2. Dough cell.

g—Glass membrane (Corning 015 glass)
p—Platinum contact
i—Platinum wire insulated with peiciene and paraffin
H—Paraffin coating as insulation on outside of glass
c—Electrode terminals
s—Peiciene seal

MacInnis and Dole type electrode with a modification of the calomel electrode described by Sorg (1929).[2]

Experimental Results

The glass electrode was calibrated by the measurement of the potential developed against a saturated calomel electrode in known buffer solutions (Figure 3). It is obvious that the glass electrode is capable

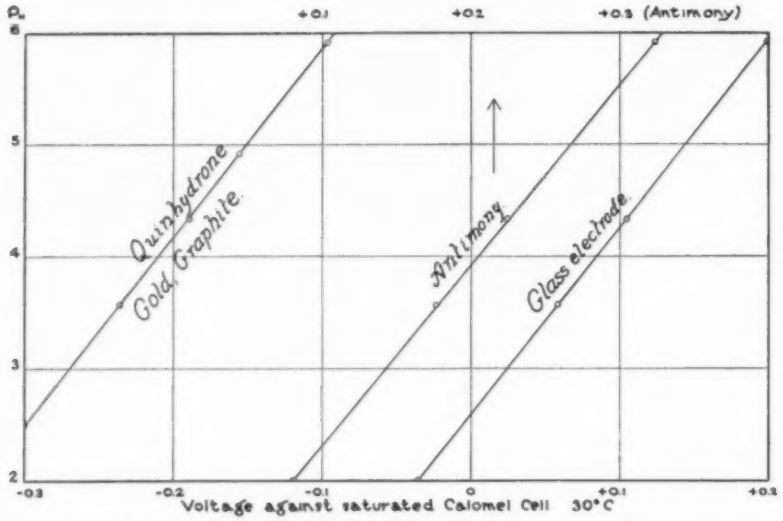

Fig. 3. Calibration of electrodes.
30° C. $E_{gh} = 0.2504 - 0.0602$ pH.
$E_{glass} = 0.3546 - 0.0602$ pH.
$E_{Sb} = 0.4317 - 0.0623$ pH.
Theoretical slope at 30° C. is 0.06015.

of giving an accurate measure of the H-ion concentration of a solution, the slope of its calibration curve being the theoretical value according to the Nernst equation. The slope of the calibration curve of the antimony electrode deviates slightly from this value, as, with one exception, has been found by other investigators. (See Parks and Beard, 1932.) It is also worthy of note that the glass electrode potentials were found to be the same whether or not quinhydrone was present in the solution. The antimony electrode appeared to act partially as a noble metal and gave irregular results.

As noted by previous investigators, glass electrodes tend to give irregular results when first used; after several days, however, the po-

[2] S. B. Ellis (private communication) has developed a glass electrode which is simply made from a standard 6 mm. diameter tube of Corning 015 glass by heating a portion to redness, then quickly and simultaneously drawing and blowing to form a very thin walled section of the tube, of a diameter approximately equivalent to that of the original. The technique may be mastered after a relatively few trials. The thin section may then be severed and carefully rounded, test-tube like,—producing a remarkably satisfactory electrode for introduction into the dough.

tentials become remarkably constant and reproducible. They appear to reach equilibrium almost instantaneously, and due to the efficient insulation characteristics of the vacuum tube circuit these thick membranes seldom show the effects of polarization. The following values were obtained on replicated doughs:

pH VALUES ON REPLICATED YEAST-FREE DOUGHS

Glass electrode	Ball quinhydrone (gold)
5.536	5.52
5.530	5.49
5.540	5.51

The pH of a fermenting dough as determined with the dough cell and by the ball quinhydrone method is given in Figure 4. As the results

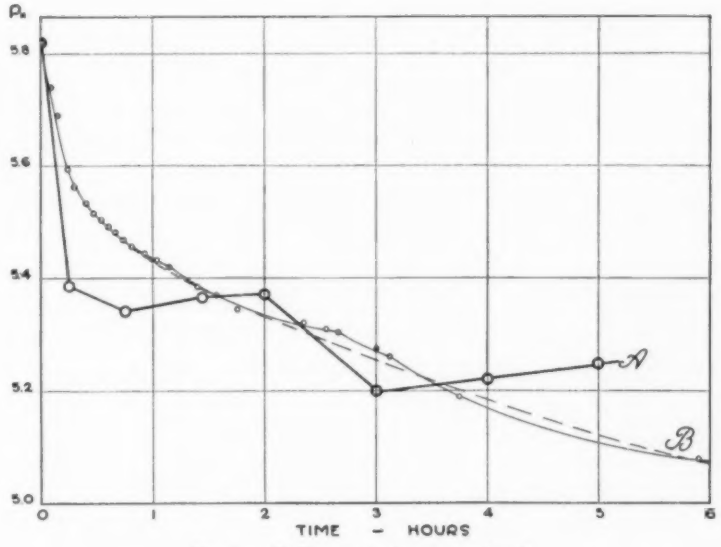

Fig. 4. pH Changes in fermenting dough.
2% yeast, 5% sugar, Northwestern patent flour.
A—Ball quinhydrone, gold.
B—Glass electrode.
(The stepwise nature of the curve has been noted several times, and is known to occur in other similar phenomena. Hence, until definitely proved otherwise, these small irregularities will be taken as actual variations. Eventually their meaning may become clear.)

of Halton and Fisher (1932) show, the values obtained with the ball quinhydrone method, while illustrating the general trend of H-ion concentration during fermentation, are slightly irregular. These variations appear to be considerably reduced by the use of the glass electrode. During the early stages of fermentation it was found that twisting the electrode slightly, presumably to bring fresh dough to the surface of the

membrane, produced a slight difference in the potential observed, sometimes as much as 20 millivolts. The pH is changing so rapidly at this point, however, that part of the discrepancy observed is due to the actual time lapse occurring between the two readings.

Summary

The development by Ellis and Kiehl (1933) of a sensitive vacuum tube circuit for the measurement of small potentials through extremely high resistance has made possible the use of glass electrodes with relatively thick and rugged membranes suitable for introduction into the dough. A glass-saturated calomel dough cell is described which seems to offer a convenient means of following the pH changes in fermenting doughs.

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THE VALUE OF DIASTATIC AND OTHER ENZYMATIC ACTIVITY IN FLOUR AND DOUGHS[1]

A STUDY FROM THE PRACTICAL SIDE

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(Received for publication April 23, 1934)

Introduction

At present there is no published comprehensive resumé on the facts in relation to diastatic or enzymatic activity in flour and doughs. Frey (1933) has summarized some essential facts about enzymes of flour in relation to yeast fermentation which, in brief, are as follows: Autolytic diastatic activity (Rumsey, 1922; see also Swanson and Calvin, 1913), as a factor in bread production is a resultant of two factors—enzyme content and starch susceptibility. Mangels (1926), Malloch (1929), and Alsberg (1924) have also researched this field. As enzyme activity is conditioned by two or more independent factors, it is obvious that a single figure index of diastatic activity can be but an approximation, and at least two indices are necessary. Enzymic activity is environmental, largely determined by harvest and milling conditions, and is not an inherent factor as has been developed by Swanson and Kroeker (1932), Halton and Fisher (1932, 1932a), Jørgensen (1931), and Kent-Jones (1924); that is to say, it is under the control of the technologist. This condition necessitates precise methods of measurement. The methods available include: (*a*) The Rumsey method, with various modifications as suggested by Malloch (1929a), and Blish and Sandstedt (1933); (*b*) The Blish precision method (Blish et al., 1932); (*c*) The punch test (Frey, 1933a); and (*d*) An extension of the Blish method (Landis, 1934).

The application of the results of such tests to practical baking problems is the next step. Sherwood and Bailey (1926), for example, state that 200 Rumsey units is a satisfactory value. Landis and Frey (1933) have developed methods to estimate the diastatic supplement required in the baking test (Short Method) using sucrose and non-diastatic malt. Blish *et al.* (1929) recommend 5% sugar for experimentally milled

[1] Read at the Tri-Section Meeting of the A. A. C. C., at Manhattan, Kansas, March 31, 1934.

flours. Studies are now under way in various laboratories to apply diastatic and enzymatic supplements.

In the average bake-shop today, the gassing power of a flour in conjunction with the determination of the maturity of a dough is arrived at by experimental testing, rather than from purely scientific testing. The average present day superintendent of a bake-shop does not know or care about the maltose figure of a flour. He is chiefly interested in obtaining a quality bread from his particular formula each day from uniform flour, making as few adjustments as necessary to suit the conditions.

The baking technologist realizes that a proper balance of enzymes is necessary to secure optimum results from flour. With a proper enzyme balance doughs are more elastic and pliable and give a more even break in the oven. Such doughs also produce loaves of considerably larger volume. This is due to the retention of the gas during the expansion period. Further, the external appearance of the finished loaf of bread has the desired symmetry and bloom.

Baker and Hulton (1908) differentiated diastase into liquefying and saccharogenic enzymes, observing that the starch liquefying enzyme either was not present in certain flours or *was unable to act*. Further observation on weak flours that were encountered showed a higher diastatic power than normal strong flours.

Ford and Gutherie (1908) in studying the behavior of diastase in the presence of normal flour proteins showed that when proteins were partially hydrolyzed with papain, a pronounced increase in diastatic activity resulted.

Sherman *et al.* (1924) claim that diastase brings about more changes at a pH of 4.4. Long found that trypsin at a pH of 5.6 and 6.3 brought about more changes. In general, enzyme action is destroyed at extremely low or high pH values, due to its lack of stability. Sherman *et al.* also state that the enzyme diastase is so inseparable from the particular protein in which it resides that it travels under the influence of electric current in either direction according to the pH of the solution. Thus, this enzyme shows a characteristic isoelectric point.

According to Sherman [2] enzyme activity has been found to depend upon keeping the protein intact, the activity being lost when the enzyme solution is subject to treatment which coagulates, hydrolyzes, or otherwise induces chemical change in the protein matter.

Katz (1933) has recently pointed out that wheats that have had a slight amount of germination before they were milled, both in viscosity and elasticity, will fall off much faster with mixing time than if the wheat had not been germinated before it was milled, because of the

[2] Sherman, H. C. Chemistry of Food and Nutrition, 3rd edition. P. 94.

proteolytic enzyme, papayotin, being present. If the fermentation is prolonged, the dough will be over-fermented, as the gluten will be too weak to hold the gas evolved, and expansion in the oven will suffer. The cell walls surrounding the carbon dioxide will tear and the gas will escape, the result being a flat loaf of bread.

Experience with sponge fermentations shows that if a flour does not possess adequate enzymatic activity, through initial poor rising, compensation must be made by the addition of diastatic or enzymatic supplements. On a straight dough, to which 3% sugar has been added, it is not so noticeable. However, a lengthening of the proof time has been observed, the oven spring is less, and the crust color of the bread is below standard. The break and shred is not normal, while the internal characteristics are less affected.

The effect of excessive enzymatic activity is usually such as to cause sticky doughs, but if the absorption be cut, a good loaf still results. The effect of extremely large amounts of enzyme is sometimes reflected in the crumb color and character, as well as in that of the crust. (See Kozmin, 1933.) The addition of too large a percentage of germinated wheat flour to the flour, or too large a percentage of diastatic or enzymatic supplements to the dough, accomplishes some of these results.

Experimental

The baking test still remains the last word in judging the practical quality of a flour in which the diastatic or enzymatic activity plays a large part.

To determine the baking value of, and additional enzymatic activity in a dough, an untreated hard winter patent flour was selected for experimentation (control flour). The break and shred of the loaves from this flour were not as smooth when baked as compared with the general average. The loaf volume was much lower than the average of current Southwest patent flours. Due to the fact that all of our flours are tested by the straight dough method, this method was selected for convenience. The experimental work to date has been confined to slight additions of germinated wheat flour and to several preparations containing hydrolytic enzymes and one enzyme which produces carbon dioxide without using free oxygen. The thought in mind was to differentiate between the values of various enzymes when added singly to the flour and baked by a commercial straight dough method under as near bake-shop conditions as was possible. Further, to study combinations of some of those enzymes that gave good results in the straight dough method, so that the results would be advantageous to the finished bread when using a minimum amount of yeast.

The basis for the addition of these products was equivalent amounts based on the converting power of each preparation containing enzymes, and a comparative test of germinated wheat flour and diastatic malt syrup based on equal Lintner value.

In Table I the loaf volumes are given for the control flour with and without treatment with a small amount of germinated wheat flour of approximately 105° Lintner. The straight doughs were fermented at three, four, and five hour periods. The increase in volume on the shorter fermentation periods was quite marked through the introduction of this amount of germinated wheat flour. The findings and scoring of the test bake and bread are also recorded. The conclusion to be drawn from these experiments is that with the increase in volume on a *shortest fermentation,* optimum results on the finished bread showed that it was also on the shortest fermentation. The maturity of the dough was speeded up by the addition of the germinated wheat flour.

In Table II are recorded the loaf volume figures for the bread in which enzyme preparations were used. It will be noticed that there has been included a dough in which a substitute was made of maltose for sucrose. One will also notice that of the loaves that contained the enzyme preparations, the volume of only one was slightly lower than that of our control, that was with diastase of malt U. S. P., which converts fifty times its own weight of starch at 40° C. in 5 minutes. The maltose dough, of course, was lower in volume. The volumes that were larger than the control were those containing clarase (chiefly diastase, but also contains maltase, trypsin, erepsin, lipase, and hemolysin), diastatic malt syrup (60° Lintner), and germinated wheat flour.

In Table II are recorded the findings and scorings of the test bakes and bread.

In observing the doughs to the machines, it was noticed that the doughs containing diastase of malt were slightly slack and the color was more creamy. Pancreatin doughs were medium slack and contained a larger amount of gas bubbles. Their color was slightly dull. The pepsin dough was slightly slack but the color was normal. Clarase doughs were slacker and slightly sticky, but their color was normal. Germinated wheat flour doughs were slightly slack but had a normal color. The diastatic malt syrup dough was slightly slack, slightly sticky, and the dough color was more creamy than the control. The dough containing diastase F was normal and similar to the control, medium slack elastic, lively, and the color was not altered, it being of a slightly creamy cast.

The bread possessed a golden brown crust color in the majority of the loaves. The crust color of the loaves that contained maltose and

TABLE I

EFFECT OF ADDITION OF GERMINATED WHEAT FLOUR TO DOUGHS

Characteristics of bread and/or dough	Flour untreated			.20% germinated wheat flour added		
Fermentation time, *Hours*	3:00	4:00	5:00	3:00	4:00	5:00
Loaf volume, *cu. in.*	105	110	109	112	113½	110
Spring, *Per cent*	29	32	31	33	34	32
Color of crust	golden brown	golden brown	golden brown	golden brown	golden brown	golden brown
Color of crumb	creamy white	creamy white	creamy white	creamy white	creamy white	slightly dull creamy
Texture	soft	velvety	velvety	velvety	soft	soft
Grain	slightly open	very close	close	close	close	slightly open
Holes	none	none	none	none	none	several
Flavor of bread	good	good	good	good	good	slightly acid
Break and shred	slightly capped	medium	slightly ragged and capped	slightly capped	capped	slightly ragged
Proof time, *Minutes*	61	60	55	62	56	53
Best developed loaves	4 hours fermentation, and 60 minutes proof time			3 hours fermentation, and 62 minutes proof time		

Absorption 60%
Loaf weights ..... 15½ oz.
Scaling weight ..... 17½ oz.
Doughs out of mixer—medium elastic.
Doughs to machines—medium elastic, lively.
Temperatures:
Doughs ..... 78° F.
Fermentation box ..... 80° F.
Proof box ..... 95° F.
Oven ..... 425° F.
Room at mixing ..... 80° F.
Room at panning ..... 80° F.

TABLE II

Effect of Adding Enzymes to Doughs

Characteristics of bread and/or dough	Control	Enzymes and/or materials added							
		Diastase of malt—105 mgs.	Pancreatin 70 mgs.	Pepsin—35 mgs.	Maltose [1] 20 gms.	Diastase "F" 35 mgs.	Clarase—35 mgs.	Germinated wheat flour 1.75 gms.	Diastatic (60 L.) malt syrup—3.19 gms.
Loaf volume, *cu. in.*	112	110½	112½	114½	107½	113	122½	116	118
Spring, *Per cent*	35	32	33	35	30	34	39	35	36
Color of crust	golden brown	golden brown	golden brown	golden brown	golden brown	golden brown	golden brown	golden brown	golden brown
Color of crumb	sl. creamy	creamy	sl. dull	sl. dull	creamy	sl. creamy	sl. creamy	sl. creamy	creamy
Texture	velvety	soft	soft	soft	velvety	velvety	velvety	velvety	velvety
Grain	very close	very open	open	open	sl. open	close	sl. open	sl. open	very close
Holes	1 small	2 small	2 small	2 medium	none	none	none	1 small	1 small
Flavor of bread	good	good	good	good	good	good	good	good	good
Break and shred	medium	capped	sl. ragged	sl. ragged	capped and ragged	badly capped	sl. double capped	sl. capped and very ragged	sl. ragged
Proof time, *Minutes*	58	59	58	58	63	58	58	61	58
Doughs to machines (all elastic)	medium	sl. slack	medium slack	sl. slack	medium	medium	slacker and sl. sticky	sl. slack	sl. slack

[1] Maltose in an equivalent amount was substituted for the sucrose ordinarily used.

Fermentation time	4 hrs.
Absorption	60%
Loaf weights	15½ oz.
Scaling weights	17½ oz.
Mixing time	8 min.
Baking time	30 min.
Doughs out of mixer—all medium elastic.	
Temperatures:	
Fermentation box	80° F.
Proof box	95° F.
Oven	425° F.
Room at mixing	80° F.
Room at panning	82° F.
Of doughs from mixers	78° F.

diastatic malt syrup were of a dark, rich brown color, while the loaves that contained pepsin had a slightly different hue but of an excellent color for the crust of a loaf of bread. The break and shred of the control loaves were from medium to a wild break, while those loaves containing diastase of malt, pepsin, clarase, germinated wheat flour, and diastatic malt syrup had a smooth break. The loaves that had maltose and diastase F in the dough had a ragged break and shell top. The latter was badly capped, while the former was only slightly capped. The bread from the dough containing pancreatin was medium smooth to a wild break and also was slightly ragged.

The summary of the entire bake can be expressed best by the conclusions drawn from the scoring of four technicians, which is as follows: The external scorings are given in sequence from best to poorest loaf of bread, *clarase, pepsin, pancreatin, diastatic malt syrup, control, diastase F, diastase of malt, maltose, germinated wheat flour.* In regard to internal characteristics given in the same manner, the sequence is—*diastase F, diastatic malt syrup, clarase, control, germinated wheat flour, maltose, pepsin, pancreatin, and diastase of malt.*

In view of the above results obtained by adding enzymes singly to the doughs, it was thought that several combinations would be advisable. In Table III are shown the loaf volumes of bread baked with the same control flour but combining some of the enzymes previously baked with additions of single enzyme preparations, such as, trypsin and zymase in the form of zymin. The bread from the dough containing added pepsin and diastase F showed a nice increase in volume as did likewise the bread from the dough containing zymin. The bread from the doughs containing added trypsin plus diastase F, and the combination of diastase F plus trypsin plus zymin suffered considerably as far as volume was concerned from excessive enzymatic activity. Of course, only one variation has been made in all these experiments, *i.e.*, they were identical as to fermentation time. The time was not changed to suit the anticipated speeding up of the fermentation.

In Table III are also given the findings of the test bake and bread. Observing the doughs to the machines, it was noticed that the doughs containing pepsin plus diastase F, and zymin alone, were medium stiff; clarase and zymin plus pepsin doughs were no slacker than the control dough; while trypsin plus diastase F doughs were very slack and very sticky, yet lively; zymin plus diastase F doughs were slightly slack and slightly sticky, yet lively; trypsin (alone) doughs were slack and slightly sticky; where the combination of diastase F plus trypsin plus zymin caused the dough to be slack and slightly sticky but was less lively than the control dough. It was further observed that the color of the doughs

TABLE III

Effect of Adding Enzymes to Doughs

Characteristics of bread and/or dough	Control	Enzymes and/or materials added							
		Pepsin + Diastase "F" 35 mgs. each	Trypsin + Diastase "F" 35 mgs. each	Zymin + Diastase "F" 35 mgs. each	Trypsin 35 mgs.	Zymin 35 mgs.	Diastase "F" + Trypsin + Zymin 35 mgs. each	Clarse 35 mgs. + Maltose [1]	Zymin + Pepsin 35 mgs. each
Loaf volume, *cu. in.*	113	117½	103	111½	113	119	104½	113	118½
Spring, *Per cent*	34	36	27	33	34	37	28	34	37
Color of crust	golden brown	golden brown	golden brown	sl. pale golden brown	golden brown	golden brown	chocolate brown	golden brown	dark golden brown
Color of crumb	sl. creamy	creamy white	dull	sl. dull	creamy	sl. creamy	dull creamy	sl. creamy	creamy white
Texture	soft	velvety	firm	velvety	harsh	soft	firm	velvety	velvety
Grain	sl. open	close	very open	close	very open	sl. open	very open	close	very close
Holes	few small	none	none	none	few small	1 large	few small	none	none
Flavor of bread	good	good	no	good	good	sl. acid	good	good	good
Break and shred	smooth and sl. capped	medium, sl. capped	ragged	smooth and capped	smooth	smooth	ragged	smooth and sl. capped	capped and sl. ragged
Proof time, *Minutes*	62	58	60	58	62	58	63	61	59
Doughs to machines (all elastic)	medium lively	medium lively	very slack and sticky, sl. dead	sl. slack and sl. sticky	slack and sl. sticky	medium-stiff-lively	slack and sl. sticky	medium-lively	medium lively
Color of doughs to machines	sl. creamy	sl. creamy	dark, dull	sl. dark	sl. dark	sl. creamy	sl. creamy	sl. creamy	sl. creamy

[1] Maltose in an equivalent amount was substituted for the sucrose ordinarily used.

Fermentation time	4 hrs.
Absorption	60%
Loaf weights	15½ oz.
Scaling weight	17½ oz.
Mixing time	8 min.
Baking time	30 min.

Doughs out of mixer—all medium elastic.

Temperatures:

Fermentation box	80° F.
Proof box	95° F.
Oven	425° F.
Room at mixing	78° F.
Room at panning	81° F.
Of doughs from mixers	78° F.

to the machines was slightly creamy except for the trypsin plus diastase F dough, and for the zymin plus diastase F dough, which were dull and the trypsin (alone) dough was slightly dull.

The loaves from the doughs to which the following had been added, pepsin plus diastase F, trypsin, zymin, and clarase, in combination with maltose substituted for the sucrose, had good external appearances, *while the zymin plus pepsin loaves appeared to have developed the external characteristics of a spring wheat flour* even to the break and shred, as well as that of a rich crust color. The inside appearance of the bread made with these additions to the dough showed that pepsin and diastase F made an excellent loaf, as well as did zymin plus pepsin. In fact, the loaf made from the dough containing clarase and the substitution of maltose for sucrose, together with the two above loaves, were much better than the control loaf of bread.

Summary

Two-tenths per cent (0.2%) germinated wheat flour (105° Lintner) was beneficial toward increasing the volume on the short fermentation periods of a straight dough. This amount of germinated wheat flour brought about optimum results in the series one hour earlier than on the control loaves. The grain was changed to a slight degree.

The addition of diastase F, by itself, showed very little action when compared with the control loaves. It was difficult to distinguish between the loaves on internal scoring. The action was held up. Quickening of fermentation, which was observed in some of the other experimental studies, was not observed with the use of this enzyme preparation.

Pepsin, used to develop proteolytic activity, was quite positive in its action.

The action of diastase of malt and pancreatin were pronounced.

The influence of clarase, combined enzymes, demonstrated itself quite markedly. The loaf volumes averaged the maximum for the series. The doughs to the machines were slacker than the control and also slightly sticky.

The diastatic malt syrup (60° Lintner) produced a nice increase in volume. The doughs to the machines were slightly slacker than the control. The internal characteristics were very good.

The addition of germinated wheat flour produced loaf volumes slightly less in size than the diastatic malt syrup loaves. However, both were larger than the control in loaf volume. The grain in the loaves from the doughs containing germinated wheat flour in this series were slightly open. The texture of the same was velvety.

The effect of another proteolytic enzyme, trypsin, showed pronounced action on the internal characteristics of the loaf. The volume and external characteristics checked very well with the control doughs.

The addition of zymin, containing the enzyme zymace, gave the largest volume loaves of the experimental series. The flavor of the loaf of bread was poor. The texture and grain further showed that the dough was slightly over-fermented. The loaves appeared to have been made from a dough in which an increment of yeast was used.

Combining of two or more of these enzymes proved more interesting than in single additions.

The addition of pepsin plus diastase F produced a better loaf of bread than the control in all respects.

The addition of trypsin plus diastase F produced some of the poorest loaves in the series. Their action was quite severe.

The addition of zymin plus diastase F produced loaves possessing a velvety texture and close grain. However, the crumb color was poorer than the control. The color of the crust on these loaves was slightly pale.

The triple combination of diastase F, trypsin, and zymin gave a good example of loss of gas retention and resulting in a flat loaf of bread.

The use of clarase (a combination itself) in a dough that had the maltose substituted in place of the sucrose, produced better loaves of bread than the control. This was especially true with respect to internal characteristics.

The combination pepsin and zymin preparation produced loaves of equal volume to that of zymin alone. However, the internal characteristics of the loaves showed a big improvement over that of zymin alone.

Acknowledgments

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EXPERIMENTAL EQUIPMENT FOR THE MANUFACTURE OF ALIMENTARY PASTES

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Durum wheats were first grown in the United States primarily because of their resistance to rust and drouth and their supposed adaptability to certain portions of the Great Plains. Very little attention was given to quality. As a matter of fact, their use for bread rather than for macaroni and similar products was emphasized, although they were never extensively used for the first mentioned purpose. The varieties first grown commercially, such as Kubanka and Arnautka, were found to be excellent for macaroni, but some of the newer varieties such as Pentad are known to be very poor. In recent years, the U. S. Department of Agriculture and the state agricultural experiment stations have been very active in producing new varieties of durum wheat, and it has been, therefore, increasingly important that some simple means of evaluating quality be made available.

Two years ago, an attempt was made to equip a laboratory for the production of macaroni on an experimental scale. This equipment with the exception of minor alterations and additions has been used for making macaroni from different varieties of wheat grown during the past two seasons. It appears to be entirely satisfactory for the purpose for which it was intended and a description of it at this time may be useful.

The equipment is fully illustrated in Figures 1, 2, and 3. Figure 1 is a front view showing the mixer, kneader, and press mounted on a table 6′ x 3′ and 3 feet high with a motor beneath. Figure 2 is a line drawing illustrating the construction details and operation of the mixer. In Figure 3 is shown the drying or curing cabinets. The mixer, kneader, press, and cabinets are similar to those used in the commercial production of macaroni but on a miniature scale.

The mixer is 5″ wide, 6″ deep, and 7″ long and is constructed with cast iron ends and sheet steel sides. Two pins ¼″ in diameter and ½″ long in the bottom of the trough prevent the dough from turning with the mixer arms. There are four mixer arm blades 1½″ wide and 1⅜″ long, mounted at an angle on the driving shaft which revolves at a speed of 36 r.p.m. The mixer arms are driven by chain drive and can be

started or stopped by a friction clutch arrangement. The mixer is so mounted that the mixed dough can be dumped into the kneader directly beneath.

The kneading mechanism consists of a kneader bowl or pan, two kneader rolls, and a plough. The pan is 10″ in diameter and 2½″ high. It is mounted on a forged steel vertical shaft. The kneader rolls and ploughs are also mounted on this same shaft. The dough pan is cast from nickel iron, smooth finished, and rests on an iron gear. The underside of the gear is mounted on roller bearings. The speed of the kneader bowl is 8 r.p.m. The kneader rolls are of the same size; one,

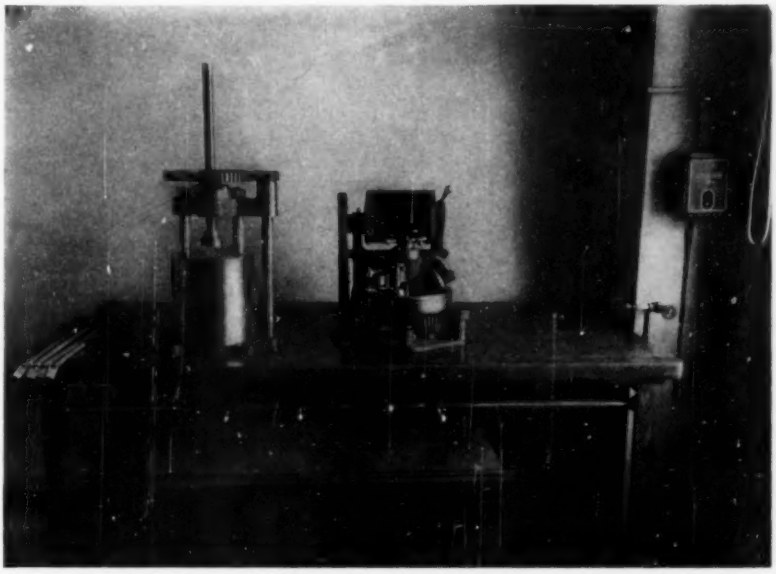

Fig. 1. Experimental mixer, kneader, and press for making macaroni mounted on a table with a motor beneath. The mixer and kneader are shown at the right and the press at the left. At the extreme left are the macaroni dies, press scraper, and sticks over which the macaroni is hung to dry.

however, is cut with 24 teeth, while the other has only 16 teeth. The pitch of these rolls is different as is shown by their position in Figure 2.

The upper end of the vertical shaft is threaded and is equipped with a nut and handle provided for raising and lowering the kneader rolls.

A plough of suitable shape, the top part of which is shown in Figure 1, is mounted on an arm extending from the shaft. A screw device is attached to the plough making it possible to adjust the distance to suit the dough conditions during kneading.

A 1½ h.p., 1800 r.p.m., A. C., 3-phase 60-cycle motor, connected to a driving shaft by raw hide pinion and cut cast iron gear, furnishes power to drive the mixer, kneader, and press.

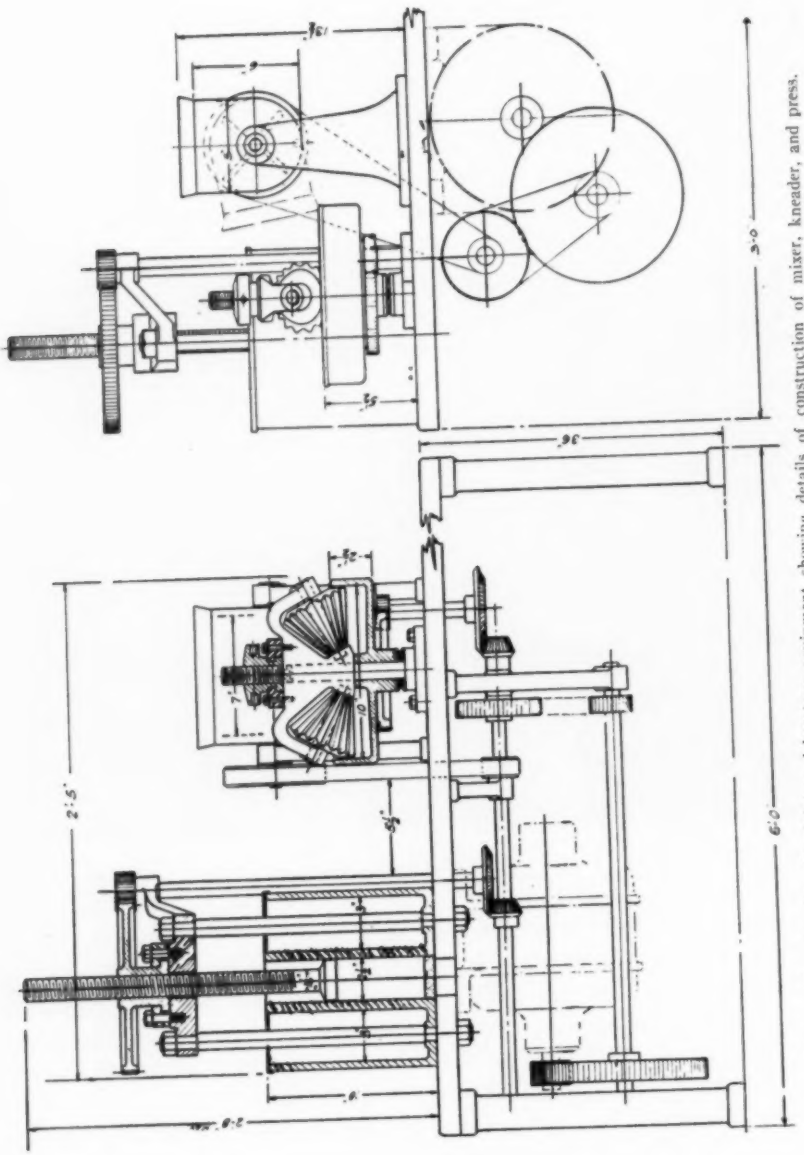

Fig. 2. Line drawing of miniature laboratory equipment showing details of construction of mixer, kneader, and press.

The press, which is 2½" x 10" in size, is surrounded by a water jacket. It also is cast from nickel iron with a smooth inside bore. At the bottom of the press is a ¼" flange on which rests the macaroni die. An electric heating element is attached to the bottom side of the water jacket surrounding the press. By this means the water is maintained at the proper temperature while the dough is going through the die. There are two levers to operate the plunger on the press, one controls its downward movement and the other its upward movement. It takes the plunger about five minutes to travel the length of the cylinders when filled with dough.

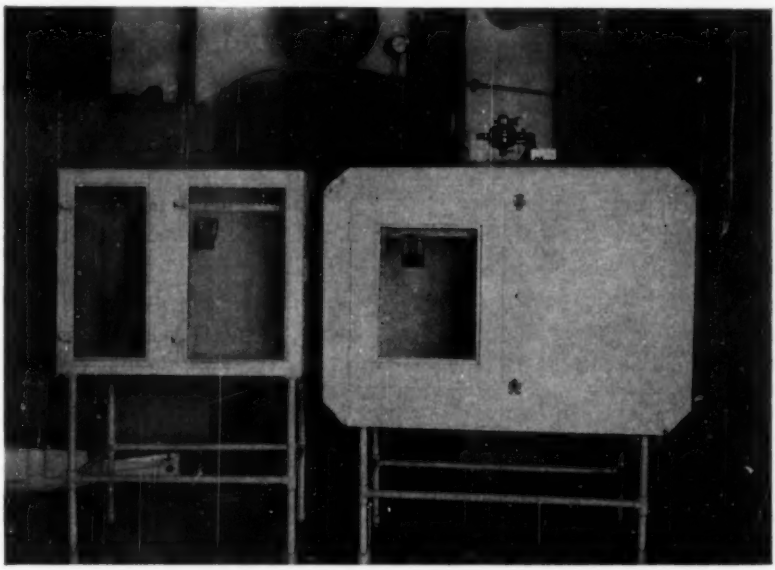

Fig. 3. Drying cabinets for curing macaroni; left, preliminary curing cabinet; right, final curing cabinet.

The drying equipment is shown in Figure 3. This equipment comprises two cabinets. In commercial practice the goods coming fresh from the press is hung over sticks and subjected for a time to a flow of heated air in order that it may be dried sufficiently to permit handling. This also takes out the excess surface moisture and prevents the macaroni from stretching. Also, if dried rapidly for too long a period, the macaroni tends to bend and the bends become permanent. To avoid this, it is usually transferred to another chamber where the drying process is completed at a slower rate.

The smaller cabinet shown in Figure 3 is the preliminary drying chamber and is equipped with an electric fan and heating coils which

circulate a current of warm air over the freshly made strands of macaroni. The moisture-laden air passes out through an opening in one end of the chamber and at the same time moisture-free air is introduced at the other end in a similar manner. This cabinet is divided into two sections by a partition—one for the fan and the other for the macaroni. A series of shutters are provided so that the current of warm air may be shut off almost entirely if it appears that the product is drying too fast. The macaroni remains in this chamber from 45 minutes to one hour, or until it starts to bend and curl, when it is taken out and transferred to the final drying cabinet.

The final drying chamber (Figure 3, right) is constructed of galvanized iron, and equipped with a fan set in such a position as to drive the air downward. The fanning process, however, is not started until about 12 hours after the macaroni has been transferred from the preliminary drying cabinet.

This cabinet is equipped with air openings on the bottom and top sides so the moist air can be expelled and dry air introduced as the drying of the macaroni proceeds.

The fan (regular wall-type with 16-inch blade) is mounted in series with a rheostat which permits the speed to be regulated from 200 r.p.m. up to its normal operating speed. By this means any degree of drying may be had depending upon the condition of the macaroni. The general practice has been to take about four days for the final drying period but this depends to a certain extent upon climatic conditions, and whether dry or humid conditions have prevailed during drying.

Both preliminary and final drying cabinets are equipped with a thermometer and a hygrometer both of which aid in securing the proper temperature and humidity during the drying process.

EFFECT OF CHLORIDE SALTS SUPPLIED TO WHEAT GROWN IN LIQUID MEDIA ON BREAD SCORES. III

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In another paper,[1] the writer discussed the effects various nitrate salts, supplied during the latter growth stage of wheat grown in liquid media, have on the quality of the protein as expressed by bread scores. The nitrate treatments were designed to have the concentration of the sap of plants during their latter growth stage relatively high in nitrogen and also in one of the following cations: ammonium, calcium, magnesium, potassium, and sodium. Grain high in protein was obtained from the various cultures, and the quality of the loaves varied with the nature of the cation used. This paper deals with bread scores obtained from wheat exposed during its latter growth period to water containing relatively large concentrations of chlorides of the five cations mentioned. Inasmuch as these salts, save NH_4Cl, supplied no nitrogen to the cultures, the grain produced was low in protein with this one exception.

A brief description of the cultural set-up employed to obtain samples for milling and baking operations was given in previous papers.[2, 3] The cultures of this series were exposed to the same cultural conditions from the date of planting (January 5) to the draining of the reservoirs of the complete nutrient solutions (April 1) as were those of the nitrate series.

In a comparison of the effects of the treatments of the two series, it should be noted that the cations whose effects on bread scores were being studied were present, and presumably absorbed, in the nitrate series simultaneously with much of the nitrogen used in the formation of proteins, whereas, in the chloride series, all the nitrogen used in the formation of protein was absorbed prior to the absorption of the cations of the chloride salts. In the former set, some nitrogen in the plant sap was in the inorganic form when exposed to the cations, but in the chloride set, nitrate had been reduced in the plant tissue owing to prior absorption, and was thus present in some organic form when the cations were ab-

[1] Effect of nitrate salts supplied to wheat grown in liquid media on bread scores. Cereal Chem. **11**: 141–152 (1934).
[2] Bread quality of wheat produced in aqueous culture media. Science **77**: 229–232 (1933).
[3] Variation of protein quality in wheat grown in aqueous culture media. Cereal Chem. **10**: 347–359 (1933).

sorbed. Before the chloride salts were supplied, the reservoirs were twice filled with water and drained to remove as much as possible of the salts of the original culture solutions which adhered to the roots, the fertilizing units having been removed at the first draining of the reservoirs. The liquid in which the cultures completed their growth was essentially a solution of a single chloride salt. Reservoirs $10' \times 2\frac{1}{2}' \times 8''$ holding approximately 500 liters of water received each 7.2 mols of the respective chloride salt.

With the exception of the NH_4Cl and the KCl treatments, the crops of the chloride treatments ripened about 10 days sooner than those from the nitrate treated series. The KCl treatment was the first to ripen and consequently was exposed for a shorter period of time to the salt solution than was the case of cultures that ripened later. In three of the chloride treatments the plants were exposed to their respective salts for about six-sixteenths, KCl about five-sixteenths, and NH_4Cl, the last to ripen, seven-sixteenths of the total culture period. The length of period of exposure of the cultures to treatment presumably affects the quantity of salts that may be absorbed, and inferentially thereby bread scores, so these variations in cultural conditions should be noted in the comparison of data of the chloride set with the data from the nitrate treatments.

All cultures save NH_4Cl produced well-filled grain, as is evidenced by the fact that the test weights per Winchester bushel exceeded 61 pounds. The grain of the NH_4Cl treatment was slightly shrivelled, a feature that might be expected in grain so markedly high in protein. Although the production of well-filled grain can be cited as evidence that the crop did not ripen prematurely, nevertheless it cannot be stated with finality that the treatments were without injury to the crop. The roots of the crops of all chloride treatments were dead before those of the check, which contained no salts during the latter growth stage. In addition to the noted early maturity of roots, the NH_4Cl culture showed some foliar abnormality. It is not known how hastened maturity, or perhaps premature death of roots affected the absorption of salts and thereby the character of the sap of the plants. As will be pointed out later in the placing of the salts by their effects on bread scores, this feature needs to be kept in mind in the interpretation of the data. The yields of grain of the chloride sets, save for the NH_4Cl treatment, were less than two-fifths of those of the corresponding nitrate salts. It was evident that the absence of nitrogen was the major factor that restricted yields, and it may be assumed that the chloride salts, if at all deterrents to yield, were operative only in a minor way. The evidence from data elsewhere obtained leads to the conclusion that exposure of the cultures for a week or ten days longer to available nitrogen would have markedly

increased grain yields without increasing their protein content, but this would have resulted in an increase of ash in the tissue, a feature intentionally avoided.

The baking data of the chloride series are given in Table I. Photographic records are also given in the several figures. The basis of comparison of the various chloride samples in the illustrations is that of the loaf from a cultural condition which provided no inorganic solutes for absorption during the latter part of the growth period of the plants. This sample produced low protein grain. Owing to the absence of all salts in the culture media during the latter growth period, it is assumed that the protein, during synthesis and translocation in the grain, was surrounded by sap markedly low in inorganic salts.

The chief deductions to be drawn from the data are as follows:

1. The culture exposed to tap water only during its latter growth stage produced grain whose bread score was without question the lowest of the series. In all elements of scoring, this loaf was clearly the poorest of the lot.

2. Comparison of the effects that absorption of an inorganic solute had on bread scores, with the effects of conditions that precluded the absorption of any inorganic solute during the latter growth period of plants, leads to the conclusion that absorption of solutes during the latter growth stage of wheat is essential to quality in bread.

3. The $CaCl_2$ treated culture produced the highest bread score of all chloride treatments comparable in protein content of their grain.

4. The NH_4Cl treatment produced the highest bread score of the chloride series. Owing, however, to the exceptionally high protein content of the grain, it needs to be excluded in the placing of the loaves. The effect of ammonium cation as a solute of the sap bathing the protein molecules could not be differentiated from the rôle it played as a constituent part of protein.

5. The placement of the loaves by the data obtained in the basic baking procedure only, of the four chloride treatments approximately alike in the protein content of their grain, is as follows: $CaCl_2$—NaCl—$MgCl_2$—KCl. When, however, consideration is given to the data obtained by the stimulated baking procedure, the above placement does not hold except for $CaCl_2$ which, again, has attained first place.

The exceptionally low bread score of culture No. 1 was apparently due to several factors. The grain was very low in protein, and consequently large loaf volume could not be expected. It was, however, not this feature alone which placed the loaf at the bottom of the series, for other treatments gave equally low protein content of the grain. The factors which control the interior character of the loaf, expressed by grain and texture, contributed to produce low bread scores. Correla-

TABLE I

Effect of the Absorption of Chloride Salts on the Bread Quality of Wheat

No.	Treatment after emergence of heads [1]	Test weight (Winchester bushel [2])	Crude protein		Ash in flour	Bread volume		Color		Texture		Grain		Crust [3]		Oven spring [4]	
			Grain	Flour		Initial	Stimulated	Initial	Stimulated	Initial	Stimulated	Initial	Stimulated	Initial	Stimulated	Initial	Stimulated
		Lbs.	*P.ct.*	*P.ct.*	*P.ct.*	*Cc.*	*Cc.*	*Score*	*Score*	*Score*	*Score*	*Score*	*Score*	*Score*	*Score*		
1	No salts to maturity	61.6	8.6	7.5	0.51	470	500	90	90	90	89	90	89	6	6	Poor	Poor
2	Solution of $CaCl_2$ to maturity	61.5	8.6	7.6	0.56	550	550	93	95	94	95	94	95	8	7	Fair	Fairly poor
3	Solution of NaCl to maturity	62.0	8.6	7.6	0.68	555	565	91	92	93	91	94	91	8	6	Fair	Poor
4	Solution of $MgCl_2$ to maturity	63.0	8.5	8.0	0.55	535	510	90	92	93	92	93	92	7	7	Fair	Fair
5	Solution of KCl to maturity	62.0	8.7	7.4	0.62	480	540	92	93	90	89	90	89	7	7	Fairly poor	Fairly poor
6	Solution of NH_4Cl to maturity	59.6	18.2	16.7	0.55	675	635	97	95	97	95	96	95	9	9	Good	Good
7	Complete nutrient solution to maturity	61.4	15.2	13.3	0.45	615	625	100	100	99	99	99	99	10	9	Good	Good

[1] All cultures were exposed to the same nutrient solution from seeding to the emergence of the first visible part of head.
[2] 2150.42 cubic inches.
[3] In the scoring of bread for crust, 10 is the designation for "ideal crust" for bread purposes.
[4] Nine grades are used by General Mills Laboratory in evaluating "oven spring," which are as follows: very, very good; very good; good; fairly good; fair; fairly poor; poor; very poor; very, very poor. Good is considered as average quality.

tion between the protein content of grain and bread scores (chiefly volume of loaf) is a justification for the practice, carried out in some markets, of using the protein content of wheat as a factor in arriving at price. Bailey [4] has shown the form of the curve, expressing the rela-

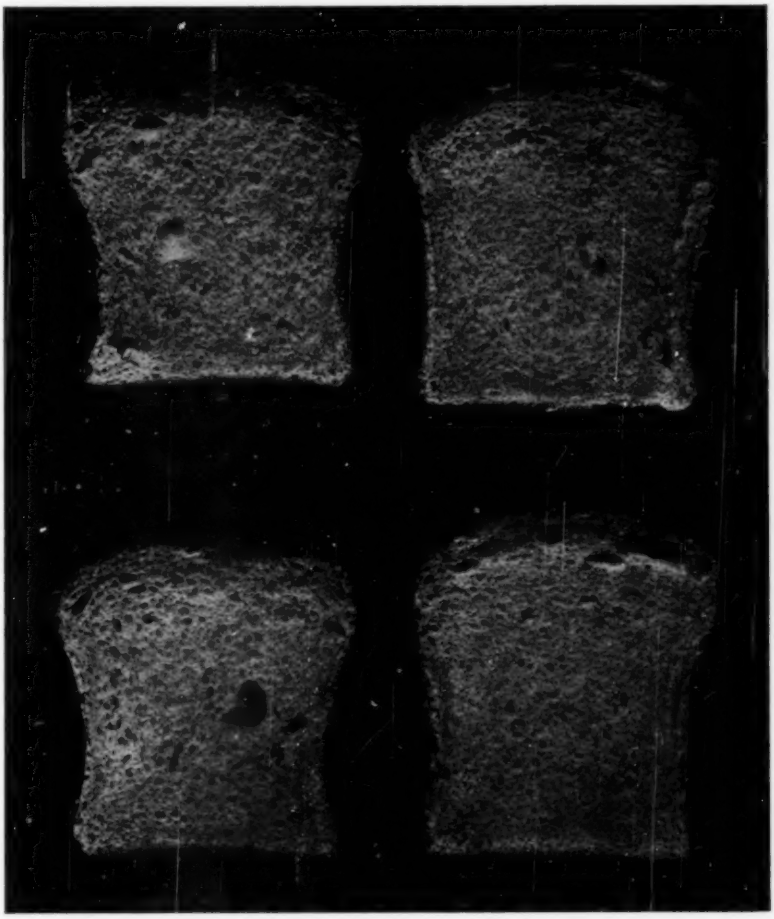

Fig. 1. Lower left (Sample No. 1, Table I). No salts during latter growth period. Lower right (Sample No. 2, Table I). $CaCl_2$ latter growth period. Upper left (Sample No. 1, Table I). No salts during latter growth period. Upper right (Sample No. 3, Table I). NaCl during latter growth period.

tion as being logarithmic rather than linear, and consequently it is necessary, in order to express one as a function of the other, to use an exponential factor to account for the gradual divergence in the relation from a straight-line character of correspondence. Volume is essentially the aggregate dimension of the size of interior structural units of a

[4] Bailey, C. H. Report of operation, State Testing Mill, Crop Season of 1922. Minn. State Dept. Agr. Bull. 34.

loaf, so variation in the cubical dimensions of loaves would ensue from differences in the size and organization of their structural units. These differences are assumed to be caused by variation in the physical state of the protein molecules arising out of the diverse character of the sap surrounding the molecules, or certain aggregates thereof, during the

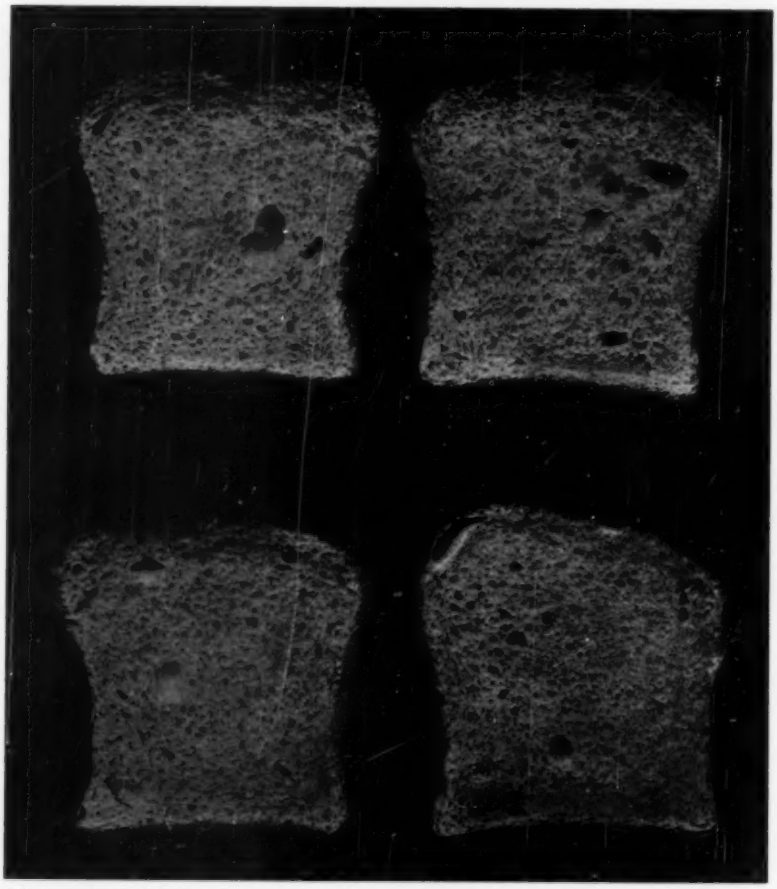

Fig. 2. Lower left (Sample No. 1, Table I). No salts during latter growth period. Lower right (Sample No. 4, Table I). $MgCl_2$ during latter growth period. Upper left (Sample No. 1, Table I). No salts during latter growth period. Upper right (Sample No. 5, Table I). KCl during latter growth period.

course of their syntheses and translocation into the grain, and reflect the cultural treatment to which the growing crop was exposed. With no inorganic solutes available for absorption during the latter growth stage, the sap of culture No. 1 became relatively dilute. The synthesis of protein (and starch) was not inhibited by this dilution, for the quantity of protein synthesized at maturity of the crop was that determined by the amount of nitrogen the plants absorbed prior to the removal of

nutrients from the culture medium. The dilution of the sap which occurred upon the growth of the plants subsequent to removal of nutrients was, however, harmful to quality of the protein. The data seem to indicate that the state of dilution of inorganic solutes in the plant sap affected the physical properties of the protein, and presumably the greater the dilution the lower the bread scores. No data are available to support such a view and although not impossible to obtain, it is probably more difficult to secure experimental material of various concentrations of plant sap than it is of saps of diverse compositions. The exceptionally low bread score of this sample, on the one hand, and the

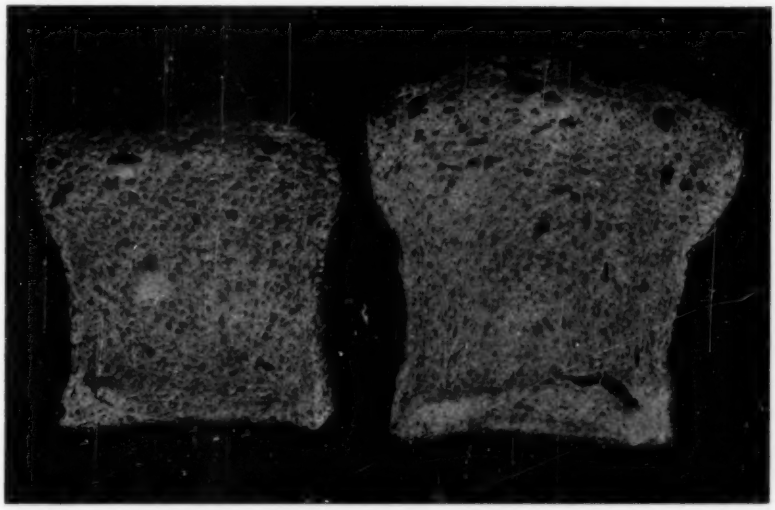

Fig. 3. Left (Sample No. 1, Table I). No salts during latter growth period. Right (Sample No. 6, Table I). NH_4Cl during latter growth period.

improvement in bread obtained by the addition of any chloride salt to the culture medium, on the other hand, appear to warrant the assumption that within limits variations in bread scores are correlated with concentrations of the plant sap.

In nature, the conditions exemplified in treatment No. 1 are rarely, if ever, attained. When nitrogen becomes deficient in soils during the latter growth period of wheat, the concentrations of available cations in soils are usually lowered but not wholly depleted. Complete removal of all solutes in a soil solution presumbaly cannot occur, although there may be some soils in which a fairly good approximation of the cultural state indicated by treatment No. 1 is obtained. It is thus assumed that the low bread score of this treatment cannot be obtained in nature, and hence the bread score is about the lowest that can be secured with this variety of wheat.

$CaCl_2$ treatment produced the highest bread score of all low-protein samples. Thus, in the low-protein series, as in the high-protein series, calcium stands at the top of the list of cations in beneficial effect on bread scores. Furthermore, comparison of the score obtained by the basic baking procedure with that of the stimulated method confirms the above placing and thus stamps calcium as unique among the five cations used. In both the high-protein wheat obtained by supplying $Ca(NO_3)_2$ to the growing crop during the latter growth stage, and in the low-protein wheat due to $CaCl_2$ treatment, the results were the same by the stimulated treatment as by the basic method. No other element has been found to possess this high order of constancy in the various features of the score.

Fig. 4. Left (Sample No. 1, Table I). No salts during latter growth period. Right (Sample No. 7, Table I). Complete nutrient solution entire growth period.

No definitive placing is warranted for NaCl, $MgCl_2$, and KCl treatments from the data so far obtained. The scores obtained by the basic procedure appear to suggest the order as NaCl, $MgCl_2$, and KCl. The scores obtained by the stimulated baking procedure, however, impair the validity of the above order. For the chloride series to have verified the placing given the cations in the nitrate series, it was necessary for KCl to follow $CaCl_2$. It is to be noted that the sample from the KCl treatment was the only one in the chloride series which showed significant gain in bread volume by stimulation. As volume is one of the more important features of a score, the marked improvement obtained in the KCl treatment, due to stimulation, leaves the question unanswered as to the proper place of potassium in its effect on bread score in the chloride series.

The complications in the experimentation, arising out of the probable premature death of the roots, needs to be considered in the interpretation of the data. The high test weight for the grain indicated that no vital process in wheat production was destroyed by these severe treatments. But as the rate of ripening affects the length of time protein and starch are susceptible to the influence of a salt solution, it is conceivable that less drastic treatment may have altered the score. Hastened maturity presumably has less beneficial effect on quality than late maturity, so far as mere salt effects on the physical states of protein are concerned. But hastened maturity, because of restriction of the quantity of carbohydrate material translocated into the grain and consequent increase of the protein content of the grain, should inferentially improve bread scores.

FACTORS INFLUENCING THE APPARENT SHORTENING VALUE OF A FAT

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During a comparative study of the shortening value of fats with a Bailey shortometer,[1] observations were made which indicated that manipulative factors might cause greater variations in breaking strength than different fats. Therefore, certain of these factors were investigated. That the results may be of interest to a fairly large group is shown by the recent recommendation that a subcommittee of the American Association of Cereal Chemists be appointed to prepare a chapter on examination of shortening materials for their revised book of methods.[2]

The factors investigated were (1) the effect of approximately minimum as against maximum creamed volume of fat and sugar,[3] (2) incompletely as against well-mixed dough, (3) rolling without any added flour (accomplished by rolling between two pieces of waxed paper) as against the minimum necessary to prevent sticking when the rolling pin is placed directly on the dough, and (4) beating into the dough the same amount of flour as had been used previously in flouring the rolling pin.

[1] Bailey, C. H., An automatic shortometer. Cereal Chem. 11: 160–163 (1934).
[2] Mangels, C. E., Report of the Committee on Methods of Analysis. Cereal Chem. 10: 470–471 (1933).
[3] This particular factor was investigated at the request of Miss Jennie D. Fisher, of the Institute of American Meat Packers.

Experimental

A modified shortbread was used. The ingredients were 110 gms. of a commercial hydrogenated lard, 125 gms. of granulated sugar, 70 cc. of water, and 300 gms. of cake flour (plus, in most cases, approximately 24 gms. for flouring the rolling pin). The method of mixing which served as a basis for the variations was as follows:

Method

The ingredients were brought to a temperature of 21° C. before mixing. The room was kept as nearly this temperature as possible. The fat was creamed at second speed in a Kitchen-aid mixer for 1 minute, the sugar added gradually during the next minute and creaming continued for 5 minutes longer. This produced a very fluffy creamed mass having approximately the largest volume which this particular fat and sugar, in the proportions used, was capable of yielding. One third of the flour and the water were beaten in at first speed for 1 minute, the remaining flour added, and beating continued for 45 seconds at the same speed. This produced a well-mixed dough. The beater was momentarily stopped four times during the mixing period—at the middle and end of the creaming in order to scrape the creamed mass back into the bottom of the mixing bowl, and during the addition of each portion of flour. The dough was stored in tightly covered, well-filled bowls overnight, during which time it came to a temperature of 9° C. It was then divided into fourths. Each fourth was successively transferred to a sheet of waxed paper and rolled with a lightly floured rolling pin to a uniform thickness of $\frac{3}{32}$ of an inch, then cut into wafers $2\frac{1}{8}$ by $1\frac{3}{8}$ inches, and baked on aluminum baking sheets in a gas-oven equipped with a Lorain regulator at 380° F. for 7 minutes. This procedure produced crisp, thoroughly baked wafers, but ones with centers of a very light tan, approximately the color known as "new silver," [4] and edges of a darker tan, "gold leaf." The wafers were cooled for 14 minutes in the room, and stored in air-tight containers for 24 hours.

The average breaking force of each batch of approximately 60 and of the total thousand wafers prepared by this method is given in Table I. The frequency curves drawn from them (and also from all the data given in this paper) are normal according to Pearson's Chi-square criterion.

The effect of the first factor investigated, that of creaming, was found by preparing a second thousand wafers made in the same way as the first except that the fat and sugar were creamed to the smallest volume consistent with mixing. This was accomplished by changing the speed of the beater during creaming from second to first speed, and by reducing the last creaming period to 4 minutes. The volume of the creamed mass was determined by displacement of cold alcohol by a 15-gram sample. The results are given in Table I and summarized in Table II. As will be seen, the difference in the specific gravity of the creamed fat and sugar, here an average difference of 0.13, did cause a significant difference in the force required to break wafers otherwise prepared alike; the fluffier, better-creamed mass produced wafers having on the average a breaking strength of 2.6 ± 0.13 ounces less than the non-fluffy mixture. This would seem to indicate that in comparing the

[4] Maerz, A., and Paul, M. Rea. A Dictionary of Color. McGraw-Hill Book Co., New York (1930). Plate II, p. 44–45.

TABLE I

THE BREAKING STRENGTH OF WAFERS PREPARED BY A STANDARD METHOD AND BY VARIATIONS FROM THIS METHOD

(Each figure for breaking strength is an average for about 60 wafers)

Standard Method[1]		Variations from the Standard Method				
		Fat and sugar barely mixed together				
Specific gravity of creamed fat and sugar	Breaking strength	Specific gravity of creamed fat and sugar	Breaking strength	Dough incompletely mixed	Dough rolled without added flour	Extra flour mixed into dough
	Oz.		*Oz.*	*Oz.*	*Oz.*	*Oz.*
0.54	29.9	0.70	30.8	33.3	17.3	24.4
0.60	28.7	0.68	31.4	33.8	16.6	23.2
0.56	30.5	0.73	31.0	33.4	16.9	21.3
0.58	29.1	0.70	31.4	34.7	16.4	23.6
0.61	30.5	0.71	30.5	33.5	17.1	23.7
0.57	31.3	0.70	31.0	31.8	16.4	23.9
0.57	29.9	0.72	30.9	34.2	16.9	24.1
0.57	29.2	0.74	31.6	31.8	16.9	24.0
0.56	30.7	0.73	30.8	32.0	16.0	24.1
0.58	30.2	0.68	31.4	32.0	16.4	24.0
0.57	29.5	0.65	31.6	32.5	16.3	24.0
0.57	30.5	0.73	31.1	31.6	16.2	23.9
0.56	30.2	0.68	31.1	29.7	16.1	24.2
0.57	30.6	0.73	31.0	30.9	15.9	24.0
0.57	30.6	0.74	31.4	30.8	15.7	24.0
0.59	28.8	0.74	31.8	30.5	16.1	24.6
0.57	30.1	0.70	31.7	30.7		25.1
0.55	29.2					
0.57	31.1					
Mean[2]						
0.57	29.9	0.70	31.2	32.2	16.4	23.9
Mean[3]	28.1 ± 0.11		30.7 ± 0.07	31.7 ± 0.04	15.7 ± 0.06	24.1 ± 0.08

[1] In this method the fat and sugar were creamed to maximum volume; the dough was well-mixed and was rolled with a lightly floured pin.
[2] Determined from ungrouped series.
[3] Determined from grouped series.

shortening value of different fats creaming to a definite specific gravity would be a fairer basis than creaming for a definite time period.

The effect of incompletely beating the dough is also shown in Tables I and II. The only change in the method of preparing these wafers from the one already outlined was in the length of the final beating period—30 seconds instead of 45. This shorter mixing period produced a dough in which bits of uncombined fat and sugar could be seen occasionally. As may be observed by comparing columns two and five of Table I, those wafers in which the ingredients were not well combined broke at a slightly but yet significantly higher value than those well combined, the difference being 3.6 ± 0.12.

Of all the factors investigated, rolling without added flour gave the most significant results. As will be seen by comparing the data in the

TABLE II

THE EFFECT OF VARIOUS MANIPULATIVE FACTORS UPON THE BREAKING STRENGTH OF WAFERS

Manipulative factor	Effect of manipulative factor[1]
Barely mixing as against thoroughly creaming the fat and sugar	$+2.6 \pm 0.13$
Incompletely as against thoroughly mixing the dough	$+3.6 \pm 0.12$
Rolling the dough without flour (*i.e.*, between pieces of waxed paper) as against the minimum necessary to prevent sticking	-12.4 ± 0.13
Mixing the flour, previously used in rolling, into the dough	-4.0 ± 0.13

[1] Reported as the difference between the average breaking strengths of 1000 wafers prepared by the standard method and by the variations. (+ indicates a toughening effect, — a tendering.)

next to the last column of Table I with those in the first, the average breaking strength of these wafers was only slightly more than half as great as those rolled with a lightly floured pin—16.4 as against 29.9 ounces.

This difference was so marked that immediately the question presented itself as to whether it was caused merely by the presence of extra flour or whether the distribution of that flour also influenced the results. Another thousand wafers were therefore prepared, this time with the quantity of flour previously used on the rolling pin beaten into the dough. As may be seen from Table I the breaking strength of these wafers lies between those in which the flour had been used on the rolling pin and those to which no extra flour had been added, but is nearer the former than the latter. This would seem to indicate that both the amount and the distribution influenced the breaking strength, but that the amount was the more important factor.

Summary

Certain manipulative factors which had been suspected of influencing the breaking strength of sugar wafers were tested with a Bailey shortometer. Creaming of the fat and sugar to the maximum volume of which this fat (a hydrogenated lard) was capable produced wafers slightly but significantly more crisp than creaming to a minimum volume, the difference in breaking strengths being 2.6 ± 0.13 ounces. Thorough, in contrast with incomplete mixing of the dough had approximately the same effect, the difference here being 3.6 ± 0.12. Rolling without flour produced markedly more tender wafers, ones in fact with breaking strengths only a little more than half as great as rolling with the minimum necessary to prevent sticking, 15.7 as against 28.1 ounces. Beating extra flour into the dough gave a more tender product than using it in rolling, but a less tender one than omitting it altogether.

BOOK REVIEWS

Calculation and Interpretation of Analysis of Variance and Covariance. By George W. Snedecor. Published by Collegiate Press Inc., Ames, Iowa, 1934. 96 pp. Price $1.00.

This small volume of illustrations of the application of Fisher's variance technique represents a serious effort to give a succinct statement of a subject which has many complexities. The method of instruction hinges upon the analysis of 12 typical problems of advancing degrees of complexity. The methods of calculation are given in rather full detail, and brief discussions of procedure, interpretation, and points in the theory are given as a part of each illustration. One's appreciation of the utility of the method of variance analysis in small sample work is certainly stimulated by a perusal of this book. A very handy table of 5% and 1% points in terms of the ratio of variances instead of the logarithmic transformations is given in the final pages, together with a valuable set of references. It is worthy of note that authoritative opinions have been given (*e.g.*, Tippett) that the 5% and 1% points are to be accepted as being merely approximations to the 10% and 2% levels of significance.

In the judgment of the reviewer, the objective of simplicity has been achieved mostly in the unfolding of the computational procedure. This, in itself, is a contribution of no mean value. However, had it been accompanied by a clear presentation of the fundamental principles of the analysis of variance, enabling readers to follow the discussional and interpretational sections with a clearer perception of what is involved in general, the value of the compilation would have been enhanced tremendously. One recalls the words of Francis Galton: "It is always well to retain a clear geometric view of the facts when we are dealing with statistical problems, which abound in pitfalls, easily overlooked by the unwary, while they are cantering gaily along upon their arithmetic."

A few unfortunate errors have been detected in formulas and calculations, and some statements of fact or theory (*e.g.*, "the analysis of variance may be used with confidence unless some rather startling lack of normality is known or suspected") are open to question. One encounters some confusion in the use of the terms "interaction," "experimental error," and "residual variance," each of which might well be specific in application. It is also a somewhat disturbing outcome of the effort to make the manual as brief as possible, that one must continually refer to other pages (usually yet to be read) to find the answers to questions raised.

The work pre-supposes some knowledge of the statistical measurement of variation by means of the standard deviation and standard errors, although no previous experience with the analysis of variance is called for. Cereal chemists would undoubtedly find it helpful to study Goulden's article in this Journal (Cereal Chem. **9**: 239–260) as a preliminary. The cautious reader who labors at each point until the reasoning becomes absolutely clear, will find himself educated adequately in the method to apply himself effectively to the analysis of many types of problems.

A. E. Treloar.

Die Getreidespeicher (Granaries). By J. K. Hoffmann and K. Mohs. Verlag Paul Parey, Berlin, 1934. 394 pp. 462 illus. Price R.M. 27.–, bound.

The first volume of this work has been reviewed in Cereal Chemistry **9**, 173 (1932). The present publication is a complete revision of Hoffmann's book, which appeared in 1916. Assistance has been offered by C. A. E. Muller, Bohnsack and Steinmetz.

Part I gives an interesting historical introduction, which is followed by the 70 pages of Part II, including the various types of elevators—wooden, stone, reinforced-concrete, and steel, with a chapter on the aeration of bins. Another chap-

ter is on storage on floors. Details are given of an Italian sack silo. It is shown that a saving of approximately 30% can be made by this method when compared with other methods of handling sacks. The pressure tests on silo walls and foundations made by Roberts Janssen, Prante, Jamieson, Bovey, Lufft and Preissner, as well as more recent experiments by Lufft on the discharging of grain out of bins are included. Examples are given of the results of faulty constructions and explosions.

The machinery for transporting grain is discussed in Part III (126 pages). Among methods of vertical transport no mention is yet made of chain conveyers. For horizontal transport, spiral and chain conveyors are treated in a few pages, whereas belt conveyors occupy more space than in the original edition. Chutes and distributors are also classified under "horizontal." There is a chapter on sack transport. The section on the unloading of grain includes: cranes, grabs, floating pontoons, bucket elevators and pneumatic transport with the necessary pumps and tubes. Weighing machines from the simple types to automatic grain weighers are to be found under machinery for control work. A few words are added on thermometer systems, on the measurement of the height of the grain column in silos and on an automatic volumeter. 30 pages are devoted to cleaning machinery—dust collectors, separators, rotating cylinders, discs, sifters, scourers, magnets and washers.

Part IV takes up 70 pages. Types of elevators and the machinery for special purposes are discussed. Almost exclusively German buildings are mentioned under farmers', cooperative and mill elevators. More attention is devoted to harbour elevators than was given in Hoffmann's original book. The terminal elevator at the Rumanian port Constanta, with a storage capacity of 100,000 tons, and another at Genoa, are treated at length. This closes the technical portion of the work. The drying of grain now forms part of Volume 1.

Part V is new (100 pages). The economical aspect of grain transport and storage. Calculations of the costs of handling grain by manual labour, cranes, sack and bucket elevators and by pneumatic means are given. The comparisons are shown in many graphs. To determine the most economical storage system the space question, building, labour, power costs and amortization are taken into consideration.

The main interest in the book to the American reader will be to get acquainted with the progress made by German firms in the construction of elevators and the equipment that these necessitate. His own up-to-date buildings and machinery are hardly referred to.

The authors have been successful in bringing together a great deal of useful information on the subject. The book has been planned to avoid unnecessary repetitions and is written in clear language. The text and the numerous illustrations are extremely well printed.

EDWIN ZIEGLER.